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FINAL REPORT NO. 60653

STATIC ELECTRICITY RESEARCH PROJECT

SCE NO. 8984

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Submitted by:

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EXECUTIVE SUMMARY

Safety Consulting Engineers, Inc. received a request from the API committee on Safety and Fire Protection to conduct a research project on static electricity ignition hazards related to the petroleum industry.

The purpose of the research project was to:

(a) Analyze technical data and information contained in the API RP 2003 and substantiate static electricity practices made therein.

(b) Compare API RP 2003 with standards/practices on static electricity written by other associations.

(c) Identify electrostatic ignition hazards in the petroleum industry not covered by API RP 2003.

(d) Identify areas that require further research.

A very detailed and exhaustive literature search was performed. Over 200 publications on electrostatics in Safety Consulting Engineers' library were reviewed to determine which references needed to be collected. Literature was also searched for in books, journals, symposia, other standards, codes, regulations including governing bodies and associations in England and Germany. Information collected was used to substantiate recommendations in API RP 2003. A comparison is made in tabular form of what is in API RP 2003 and how it is substantiated by the literature.

Recommendations made in API RP 2003 were also compared with recommendations and standards of other organizations within the context of the petroleum industry. Comparisons were made for

completeness in practice. There is good agreement between API RP 2003 with other standards, however, there are differences and further research is necessary.

Literature was also reviewed for sources of information on current uses of plastics in the petroleum industry. Key people in the petroleum industry were contacted to determine the uses of plastics in the industry. Some of the general concerns were in the use of underground plastic tanks at service stations and if it was acceptable to use nonconductive vacuum hoses during tank filling operations.

Some of the conclusions drawn during this research project are:

- For liquids of very low conductivity (less than 2 pS/m) the 30 second residence time downstream of a filter is not very conservative. It should be increased to 100 seconds. This has been proved theoretically and is verified in published work.

- Plastic containers and equipment are responsible for many fires and injuries. Incidents of tank explosion have occurred during the splash filling of conductive liquids. Plastic tubing and small sample bottles have also contributed to fires in the handling of conductive liquids. Further research is needed in the use of plastic in the petroleum industry.

- Personnel grounding is a direct or indirect cause of hose fires during filling of tanks with flammable gas mixtures in most easily ignitable concentrations. Clothing is usually not a problem unless it is removed causing crackling discharges. Further research is recommended.

Standards need to be developed for the safe use of plastics in the petroleum industry. Certain areas of API RP 2003 require additional coverage including the use of plastics, static generation on clothing and surfaces, fiberglass storage tanks and

effect of various coatings on tank surfaces. The following are some of the areas where further research is recommended:

- Determine whether inner nonconductive sleeves in pipes and hoses are a brush discharge hazard during hose drainage and whether antistatic hose lines are needed in nonconductive liquid service.
- Theoretical and experimental studies on the effects of nonconductive and semiconductive lines and excess charge at free liquid surface and the possibility of propagating brush discharges.
- To determine if it is safe to use filters when filling conductive and semiconductive liquids into lined tanks and drums.
- Conduct a full scale experiment on a tank truck filled with a high flash point mineral oil using a pipe or composite "rough bore" hose. The measure of streaming current would determine whether such hoses are contributors to fires.

I. INTRODUCTION

Safety Consulting Engineers, Inc. (SCE) has prepared this report for work on the Static Electricity Research Project which was administered by the American Petroleum Institute's Committee on Safety and Fire Protection (COSFP). This project was performed in three phases:

Phase I: The technical data and information contained in API RP 2003, Protection Against Ignitions Arising Out of Static, Lightning, and Stray Currents, March 1982, validated to substantiate the recommendations made therein.

NOTE: Since a new version of API 2003 has been released, some issues may not apply.

Phase II: Areas that are relevant to electrostatic ignition hazards in the petroleum industry but are not covered, or are inadequately covered in the existing version of API RP 2008, were identified and documentation was provided where it exists for these areas.

Phase III: Areas from Phase I or Phase II that require further research were identified and research programs for these areas are proposed.

A. Background

Phase I

Recommendations stated in API RP 2003 are guidelines followed in the petroleum industry for protection from electrical ignition of flammable vapors due to static, lightning and stray currents. API RP 2003 is based on research and many years of practical experience in the industry. Some substantiation of the recommendations given in API RP 2003 has already been documented through COSFP's Technical Data Recovery Project and other technical

literature. However, many items may require further research to substantiate, such as the use of plastics and other nonconductive equipment.

Phase II

Certain areas of API RP 2003 may require additional coverage, including the use of plastics, static generation on clothing and surfaces, fiberglass storage tanks, and effects of various coatings. Static charges are generated during the flow of fluids and can be a concern with low conductivity fluids that may come in contact with flammable vapor/air mixtures. While earthing is the primary means of protection from incendiary discharge for systems with metallic conductors, it is ineffective when nonconductive plastic pipes, storage containers, sheets, coatings, liners, and clothing are used. Plastics are readily charged by contact electrification and induction and can dissipate charges very slowly, depending on resistivity, thereby producing hazards from discharges from their surface or from nearby insulated conductors. Therefore, standard criteria needs to be developed for the safe use of plastics in the presence of flammable atmospheres.

Phase III

For issues and recommendations contained in the current edition of API RP 2003 or identified in Phase II of this project that were not able to be validated or resolved, additional research was identified and programs were recommended for development and implementation were needed.

II. SCOPE OF WORK

A. Phase I

1. Objectives

The objective of Phase I of this research project is as follows:

a. To substantiate the static electricity recommended practices outlined in API RP 2003 using internal API documents and any technical information from published sources.

b. To compare API RP 2003 with static electricity practices written by other associations and governing bodies and identify areas of differences and provide substantiation of these differences.

III TASK PLAN

(A) Literature Search

The literature was searched for books, journals, papers, symposia, and task force reports containing information useful in substantiating the recommendations made in API RP 2003. This search included other standards, practices, guidelines, regulations, codes, and methods published by other associations and governing bodies.

Applicable documents from API, including those from COSFP's Technical Data Recovery Project were reviewed.

A computer search was performed at Safety Consulting Engineers, Inc. (SCE) using NTIS, Chemical Abstracts, Physical Abstracts, and IQuest Literature Service.

A quick review of all materials collected, including the over 200 publications on electrostatics in Safety Consulting Engineers' library and the libraries of Laurence Britton were performed to determine which references need to be collected from

libraries or publishers.

The following libraries were utilized to find the needed publications: The John Crerar Library, Northwestern University Engineering and Science Library, Illinois Institute of Technology Technical Library, Purdue University, University of Minnesota and the Wisconsin Physics, Chemistry and Engineering Libraries.

Governing bodies and associations, in England and West Germany were contacted to obtain codes, standards and regulations used in control of static electricity, lightning and stray currents.

A summary of all literature reviewed is found in Appendix D. Monograph.

(B) Literature Comparison

Experimental data, mathematical models, and scientific calculations were used to substantiate the recommendations in API RP 2008. Substantiation was as exhaustive as possible, within the constraints of the literature search performed in Part A.

As each section of API RP 2003 was reviewed, documents were analyzed as to how reliable the information is and how the information pertains to the recommendations of API RP 2003. A summary worksheet was prepared which briefly described what is in API RP 2003 and how it is (or is not) substantiated by the literature. The results are shown in Appendix A.

(C) Standards Comparison

The recommendations made in API RP 2003 were compared with recommendations and standards of other organizations within

the context of petroleum operations. The comparisons were made with regards to completeness and any conservatism present in the recommendations of API RP 2003. Differences in the practices were identified and substantiation of these differences was made wherever possible using the results of Part B.

Each section of API RP 2003 was compared to other standards using the information for substantiation from Parts A and B.

As each section was compared, a summary worksheet was prepared showing briefly what the differences in the standards are and how the differences can be resolved using the literature.

The National Fire Protection Agency recommended practices on handling and processing of flammable liquids (NFPA 30), control of static electricity (NFPA 77), and protection from lightning (NFPA 78) were compared to API RP 2003. Codes from the British Standards Institute ("Code of Practice for Control of Undesirable Static Electricity", BS5958), and the "Chemistry" Committee of the Chief Federation of the Industrial Trade Associations Center for Accident Prevention and Industrial Medicine from West Germany) ("Guidelines for Avoiding Danger of Ignition As a Result of Electrostatic Charges") were also compared. Other codes and standards include Chapter 7 on "Static Electricity" in the Army Safety Manual DARCOM-R 385-100, and National Safety Council Data Sheet 547. The standards comparison results are shown in Appendix B.

(D) Monograph

A monograph was prepared documenting the substantiations of API RP 2008 made in Task B and the comparisons made in Task C. The monograph was written in practical, tutorial terms for use by engineers and engineering managers in the petroleum industry. The monograph follows the order of subjects in API RP 2003 and a bibliography of material for further reference which was developed using the information management program. All substantiations and comparisons were traceable to the originating literature. Areas requiring further research were identified in the monograph. The monograph is found in Appendix D.

(E) Nonconductive Materials Study

(1) Objectives

The objectives of Phase II of this research project were as follows:

a. To characterize the electrostatic hazards associated with the use of nonconductive plastics in the petroleum industry.

b. To establish a well-supported methodology, with validations from existing literature, etc., of hazard identification which can be used by API committees in the development of relevant standards.

c. To identify and provide validation for other areas recommended for expanded coverage in API RP 2003.

(2) Literature Search on Plastics

The literature was reviewed for sources of information on current uses of plastic in the petroleum industry and for information on current and past work done to identify and

quantify the hazards presented by their use.

(a) Literature Sources

A computer search was performed at SCE for information on the uses and hazards of plastics in the petroleum industry. In addition, the literature was searched to identify nonconductive materials use and safety around flammable liquids.

Governing bodies and associations were also contacted in order to obtain codes, standards, regulations and practices on static electricity control when using plastics with flammable liquids.

A summary of literature sources identified is shown in Appendix C.

(b) Field Uses/Experience

Key people in the petroleum industry were contacted to determine the uses of plastics in the industry and which of the uses should be covered in API RP 2003. A summary of industry contacts is shown in Table I.

(c) Standards Investigation Comparison

Currently accepted standards on the use of plastics were investigated to determine what criteria and recommendations are now being followed in other industries and how these apply to petroleum industry operations. The investigation included identification of the hazards involved, in reference to the methods used in other industries to eliminate them.

As each standard was analyzed, a summary worksheet was prepared which briefly showed what methods are used

TABLE I

SUMMARY OF INDUSTRY CONTACTS

COMPANY	SUBJECT	COMPANY PRACTICE
Conoco Oil	Use of Plastics	Sometimes are used They have many criteria to determine if non-metal material is to be used They do not use (FRP) plastic on truck Had one incident with a plastic tank awhile ago
ORYX ENERGY CO.	Use of Plastics	They use plastics and FRP tanks up to 80 gal size in exploration Not much in production they have a program to evaluate arcing during repair of PVC tube stock
Union Pacific Resource	Use of Plastic	They lost a salt water nonconducting tank to lightning They use small nonconducting containers for tank bottom material Also had underground tanks (Slop condensate) Tank hit by lightning
Unocal Calif	Use of Plastic Around Flammable Liquid	Nothing standard across company In oil and gas production, small (FRP and plastic) tanks (80 gal) used for additives and water Also use plastic (FRP) additive tanks by cooling towers They do not use portable plastic containers for flammable liquids

TABLE I (continued)

SUMMARY OF INDUSTRY CONTACTS

COMPANY	SUBJECT	COMPANY PRACTICE
Sun Refining Marketing	Use of Plastics	They use plastics at: - Refineries, for fire water - Sour H_2O stripper - Production 3" crude lines on production trucks (well to small truck) - Pipeline crude oil 10-12" - Terminals none used - Service stations fiber glass/polyethylene tanks, unloading lines.
Amoco Oil Company	Use of Plastics by Flammable Liquids	Refining operations: - Use 55-gal poly drums max size - Repackages to smaller package Lubes packaged: in quart, gallon and 5 gallon of non-flammable liquids
B.P. America	Use of Plastics by Flammable Liquids	-
Chevron - Calf	Use of Plastics by Flammable Liquids	-
Exxon-Houston	Use of Plastics by Flammable Liquids	Referred to R. Murphy in New Jersey for response

TABLE I (continued)

SUMMARY OF INDUSTRY CONTACTS

COMPANY	SUBJECT	COMPANY PRACTICE
N.J.A. Petrochem Co.		Flammable liquids can be placed in containers up to 250 lengths: if temp. of liquid is less than 5°C below flash point and plastic has surface resistivity less than 10^{11}ohm or lining is less than 0.5 mm thick For nonconductive containers of surface resistivity > 10^{11}ohm (for liners < 0.5mm thick) all flammable liquids except CS_2 and alcohol can be placed in them if container is less than 5 liter size.

General Company Comments:

- Should vacuum truck hoses be conductive or OK to be nonconductive.
- Concerned about using plastic (FRP) tanks (underground at service stations.
- Concerned about use of braided metal or synthetic sleeve on liquid fill line.

in other industries to eliminate the hazards involved. The results of the standards comparison are shown in Table II.

IV CONCLUSIONS

While Figure 1 in API RP 2003 is a good approximation for fuels such as paraffinic mixtures with regular ASTM distillation curves, it is erroneous for many single component hydrocarbons and other flammables. A better illustration is recommended for these cases and Figure 1 should be accompanied by a use limitation statement including a caveat about mist and foam ignition. The ignition energy of mist below (about) 30 micron diameter converges with that of a vapor. Very fine mist can be produced during splash filling and as foam breaks up.

It should be noted that exponential relaxation (above 2 pS/m) is not governed solely by "rest conductivity" as measured in the laboratory. The effective conductivity in the field is significantly reduced by temperature decreases (for example from about 100 pS/m at 25°C to about 30 pS/m at -10°C). Further, highly charged liquid may display a relaxation time that is up to one order of magnitude greater than predicted (this effect is usually unimportant unless a microfilter or other source of high charging is present). To address the temperature problem, either the nominal "static accumulation" conductivity might be raised to 150 pS/m, or a temperature correction can be made. In addition, the conductivity can be measured at the temperature of interest.

The velocity-diameter limit developed experimentally for tank truck filling was developed for smooth-bore pipes and hoses during

TABLE II

STANDARDS COMPARISON
INSULATING MATERIALS IN PRESENCE OF FLAMMABLE LIQUIDS

STANDARD	DATE	SUBJECT	REQUIREMENT	COMMENTS
NFPA 77 Recommended Practice on Static Electricity	1983	Para 7-8 plastic and plastic lined containers Non-metallic containers to handle flammable liquids Para 9-8 container filling	5 - 55 gal sizes are potentially dangerous "4 - 8.5 container of glass or non-conducting materials of 5 gal or less usually are filled without precaution see para 7-8"	Hazards are not indentified or categorized This depends on the charging and drainoff characteristics of the liquid material combinations
DoD HDBK-263 ESD Control Handbook	2 May 1980	Definitions of Materials	- Insulative material Surface resistivity $>10^{14}$ ohm/square - Anti-static material Surface resistivity $>10^{9}$ to $<10^{14}$ ohm/square - Static dissapative material $>10^{5}$ to $<10^{9}$ ohm/square - Conductive material $>10^{5}$ ohms/square	Good definitions

TABLE II (continued)

STANDARDS COMPARISONS
INSULATING MATERIALS IN PRESENCE OF FLAMMABLE LIQUIDS

STANDARD	DATE	SUBJECT	REQUIREMENT	COMMENTS
BS-5958 Proposed changes	1991	Storage tanks	4.2.1 Large storage tanks completely fabricated from highly resistive materials with volume resistivities greater than 10^8ohm m or surface resistivity greater than 10^{10}ohm are not recommended for flammable liquids. Exception if liquid handling operations do not produce dangerous levels of static electricity and no charge generating process exists outside the tank.	Does not define dangerous levels of static electricity

TABLE II (continued)

STANDARDS COMPARISONS
INSULATING MATERIALS IN PRESENCE OF FLAMMABLE LIQUIDS

STANDARD	DATE	SUBJECT	REQUIREMENT	COMMENTS
BS-5958 Proposed changes	1991	Non-metallic storage tanks - underground	5.2.1 Tanks should be individually designed for each specific application. To conform to safety, max charge produced in filling of tank must not produce field strength to cause discharge.	Propogating brush discharges are a strong possibility here. Restrictions or ES charging and flowing should be better defined
			5.1 If liquid is conductive (>50 ps/m), charge will dissipate safely to earth when it is in contact with a conducting surface to ground	Immiscible liquids could compromize safety if flash point and ES charging is favorable
			9.2.2 If flammable atmospheres are possible near that vehicle tank, conductive or semi-conductive hoses should be used	Charging and flow rate also are important
			12.4.1 Highly resistive containers can be used for flammable liquids occasionally provided that the ES ignition risk is acceptable	Risk not defined

TABLE II (continued)

STANDARDS COMPARISONS
INSULATING MATERIALS IN PRESENCE OF FLAMMABLE LIQUIDS

STANDARD	DATE	SUBJECT	REQUIREMENT	COMMENT
			12.4.4. When low conductivity liquids are used, highly resistive containers up to 5 liters: are alright. Above that expert advise should be sought	This is questionable depending on liquid on mixture charging
			12.5 In continuous flammable atmospheres highly resistive containers should not be used independent of size	Good

overhead filling via a dip pipe. Products between 0.36 and 0.50 m^2/s are suggested in the literature, while higher values may be used for compartment lengths greater than 2 meters. For bottom connection filling the product should not exceed 0.36 m^2/s and the inlet should be fitted with a deflector to prevent jetting. The value of 0.5 m^2/s being used has been successful in loading typical petroleum fuel to date. Composite hoses containing an internal grounding spiral should be avoided when loading nonconductive flammables because of the excessive static generation apparently caused by the spiral, especially in hoses of small diameter. To allow for the limited test conditions under which the API velocity-diameter limit was developed (uniform charge distribution, no free water etc.), and some fires which have occurred at low product values, it should be stressed that a lower v•d product is desirable particularly for bad actors like toluene. An important point to make is that for equal values of v•d product, the maximum safe filling rate is proportional to filling pipe diameter. Where there is a choice, larger diameter pipes are intrinsically safer for a given flow rate. This is additionally important for rough bore (spiral wound) hoses where for smaller diameters the blockage ratio and charging should be greater. If rubber boots on similar devices are connected to the end of dip pipes they should be conductive and reach to the bottom of the tank, and be in contact on the bottom to avoid undue turbulance.

A potential problem with wound composite hoses is that the inner spiral is often not attached to the end connectors and in

some cases the gap is an effective spark source during draining of nonconductive liquid from the hose. To avoid this hazard, a semiconductive liner may be used. Alternatively, the hose can be designed to provide bonding via the inner spiral. To show that the inner spiral is bonded, one design uses an isolated outer spiral and other designs (such as an outer spiral bonded to a single, grounded end connector to avoid complete isolation) might be specified. Also the problem will not exist with adequate time to relax charges.

Section 2.4.2 in API RP 2003 states that nonconductive hose can be used provided the end connector is bonded. Use of nonconductive hose for nonconductive flammables can be hazardous since discharges may occur on the surface(s). At high levels of charging, such as downstream of a filter, powerful propagating brush discharges may occur. The meaning of the statement made that "continuity is not required in bottom or top loading through tight connections" is unclear. If tight means electrically contacting, the statement is correct.

Hoses (and pipe) containing a continuous nonconductive liner may undergo pinhole puncture on the lining by small propagating brush discharges when charged nonconducting liquid accumulates surface charge on the liner. This is most likely to occur downstream of filters. The problem has occurred in steel flexible hose with extruded thermoplastic liner, where repeated puncture at a point caused leakage. With composite hose containing a coated spiral any pinholes will go to this spiral rather than through the

carcass, since leaks should not be caused, the phenomenon probably has not been noticed. It is unknown whether these discharges could produce a hazard or not. This type of discharge can be avoided using a semiconductive liner (metal or carbon filled polyolefin) or any type of hose with internal bare metal surfaces such as an uncoated inner spiral.

In API RP 2003, Figure 7 shows what appears to be a close-coupled filter in drum filling and states that the hose can be nonconducting. Both can be extremely dangerous in some conditions for nonconductive flammables as is well supported by literature and by accident histories.

Purging recommendations should refer to NFPA 69 to generalize the coverage.

The 30 second residence time downstream of a filter is not conservative for liquids of very low conductivity (less than about 2 pS/m) and may have to be increased to 100 seconds. This is proved theoretically and is verified by published test work. The reason for this need is that filters generate high levels of charge even at low conductivity; even where this is not the case the charge density dependence of hyperbolic relaxation makes the time taken to relax to acceptable levels (20-30 $\mu C/m^3$) almost independent of the initial charge density above about 100 $\mu C/m^3$. Temperature effects on conductivity should be considered to make 2 pS/m a meaningful demarcation. Note that the NFPA and BS guidelines calling for "3 relaxation times" residence would require 27 seconds for a typical hydrocarbon at 2 pS/m which is close to the "worst

case" 30 seconds presently given by API. However, below 2 pS/m further analysis is necessary to deterine if 20 seconds is safe. Virtually in all cases, 100 seconds is safe.

While 50 pS/m is a useful demarcation for static accumulation in grounded equipment, it does not represent the conductivity level above which a liquid is "Conductive". This has been drawn at various levels according to the handling operation involved. A conservative "ceiling" level of 100,000 pS/m has been established. A "safe" conductivity for almost all operations, including those involving stirred slurries and pipes/hoses lined with high resistivity material has been established at 1,000 pS/m. Other levels (for example 200-300 pS/m) have been applied to certain military applications such as war planes.

Plastic containers and equipment are responsible for many fires and injuries and the present coverage is entirely inadequate. In the case of FRP and other plastic aboveground tanks, splash filling must not be done. There was a recent FRP tank explosion involving splash filling of a conductive liquid; conductive liquids give rise to surface sparks rather than brushes and only a few kV is needed to ignite vapor. It is important to stress that with plastic containers there is no safe liquid conductivity. Sparks from conductive liquids can be produced by splash filling or simply rubbing the outside of the container, which induces very high potentials in the liquid. A charged plastic surface can give rise to incendive brush discharges or may induce hazardous potentials on nearby conductors. Even plastic tubing and small sample bottles

(when handling conductive liquids) have contributed to causing fires.

In relationship to personnel grounding, there is some evidence that ungrounded personnel are a direct or indirect cause of hose fires following tanker filling in high risk situations. Personnel grounding may be required in high risk areas such as handling of liquids where flammable gas mixtures are in most easily ignitable concentrations. It is true that clothing is not usually a problem unless it is removed causing crackling discharges (brush types). The type of clothing can determine the charge on an ungrounded person, however. Personnel grounding may be achieved using a variety of commercially available devices (conductive/antistatic shoes, foot grounders, bracelets) and commercially available accessories such as conductive paint for floors, and resistance testers to ensure the devices are operating properly. In some situations, personnel grounding may be required to prevent fuel vapor ignitions.

To avoid stray currents in wharf lines an insulating flange (commercially available) should be installed. Nonconductive hose can be used providing no additional hazards can occur.

RF stray currents in the vicinity of radar and radio transmitters should be addressed. Shell has published a nomograph allowing ignition hazard field strength thresholds to be found for methane and hydrogen with respect to source frequency and the loop perimeter of any adventitious antenna.

V RECOMMENDATIONS FOR FURTHER WORK

(1) A project is recommended in which an electrically isolated tank truck (or less desirable, a tank of similar dimensions) would be grounded through an electrometer and filled with a high flash point mineral oil with a conductivity of about 2 pS/m, either through a pipe or a composite "rough bore" hose. The measurement of streaming current would determine whether such hoses are a cause of mysterious fires. Simultaneously it would be possible to use an image intensifier to observe any electrostatic discharges in the truck. An unbaffled truck would simplify this. Grounded probes could be used to simulate truck internals. Both top and bottom filling might be carried out using image intensification to verify the BS 5958 recommendation to limit bottom fill flow rates to 25% those of top filling.

(2) Research is recommended to determine whether inner nonconductive sleeves in pipes and hoses are a brush discharge hazard during hose drainage and whether antistatic hose liners (such as used by Willcox) are needed in nonconductive liquid service where spiral breakage is not present.

(3) Plastic manually-operated drum pumps are frequently used to transfer flammable liquids and there has been a report of a fire originating inside a drum. It appeared possible in this case that a brush discharge occurred from the pump handle being operated at the time, although a discharge from the operator might alternatively have occurred. The liquid was conductive. No published information has been found on drum pump hazards and some study should be made.

(4) Theoretical and experimental studies of the effects of nonconductive and semiconductive liners and excess charge at free liquid surfaces are needed. While it is unlikely that propagating brush discharges are produced on plastic liners in liquid handling systems, this possibility is considered by various authors.

(5) Filters are being used on lances when handling conductive and semiconductive liquids. Research is needed into whether this practice is safe, particularly when filling lined tanks and drums. There would appear to be a problem during the early stages of filling especially.

(6) In the Petrochemical Industry the use of lances is often limited by personnel exposure problems when handling toxic or malodorous liquids. Research is needed as to whether splash filling of lined drums is an acceptable

procedure and what the limitations (liquid conductivity, liner thickness and resistivity etc.) should be. In some cases the exposure problem can be mitigated by the use of spring-type discharge electrodes at the end of the lance, which uncoils into the liquid during flow, minimizing wetting of the lance itself. Such devices are relatively unheard of but may be purchased by special order.

(7) There have been numerous studies of brush discharges from liquid surfaces but apparently none on the formation and effective energy of the "go devil", a surface discharge that can be several feet in length and which is somewhat analogous to the "wall-to-cone" (or "Bulking Brush") discharges seen during silo filling. By analogy one might expect the effective energy to be greater than for brush discharges, perhaps around 10mJ. Such discharge might be responsible for mist ignition of high flash-point liquids.

(8) It is recommended that the industry hold discussions with container manufacturers to determine the feasibility of antistatic plastics for use in all-plastic drums and other applications. For example, conductive carbon black-loaded polyethylene may be directly bonded to an inner polyethylene drum shell allowing direct grounding while avoiding the mechanical problems of polysteel drums and retaining he advantages of a polyethylene liner. The conductive plastic will have a greater thermal conductivity than HDPE and may improve fire resistance by the Factory Mutual test. By improving the fire resistance with respect to steel drums the present restrictions on plastic drum storage might be eased. A groundable plastic drum would present no external discharge hazards and for conductive flammables could be safely loaded and unloaded using a metal dip pipe.

(9) The effect of entrained water or electrostatic charging for nonconductive material contact by flammable liquids should be studied.

(10) Detailed proposed studies will be supplied under separate cover.

APPENDIX A

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.1	Resistances of less than 1 meg-ohm may act as short circuits.	No information.		
2.3.1-2.3.3	Figure 1 shows relationship between temperature, vapor pressure, flammability limits of petroleum products.	Shows plot of Reid vapor pressure as a function of temperature for various fuels. Provides flammability limits.	Strawson Ref. #12 16	Yes
		Experiments with the flow of hydrogen carbon solutions through SS tubing to measure charging current magnitude. Measurements obtained indicate that using liquid conductivity as the only parameter by which to assess charging phenomena is misleading.	Goodfellow & Graydon Ref. #71 1267-1280	Not addressed
		Shows sample of suggested plot for benzene vapor.	Britton & Smith Ref. #1 54-55	Not addressed
		Establish most easily ignitable vapor space mixtures from vapor pressure data, especially for "bad actors."	Britton & Smith Ref. #2 201	Not addressed
		Shows sample of suggested plot for hydrocarbon vapors	Saletan Ref. #3 101	Not addressed
		Preliminary screening on basis of vapor pressures is misleading; use relationship between dielectric constant and conductivity to assess electrostatic hazard.	Saletan Ref. #4 101-102	
2.4.1	Bond resistance as high as 1 meg-ohm is adequate for static dissipation	Discusses bond resistance values offered by various agencies.	Mancini Ref. #5 27-28	Yes and No
		Resistance to earth should be less than 10 ohms for practical convenience.	Loveland Ref. #27 5	No

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMENDATION SUBSTANTIATED
2.4.1	(continued)	Summarizes earthing & bonding criteria in various zones. See Table 1.	Gibson & Harper Ref. #11 35-37	In some cases
		Resistance of no greater than 1 meg-ohm under even unfavorable conditions; when capacitance is less than 100 pF, resistances of up to 10^8 ohms are sufficient using RC=10 ms; see Case Study 2	Haase Ref. #8 60-61, 66, 71	Yes and No
	Bond wire connection is essential where high- and intermediate- vapor- pressure products are loaded through top domes.	Bond fill pipe to tank. Resistance through tires must be low enough that dangerous voltages (1500 volts or more) will not build up in system if truck is not grounded. Discusses laboratory study done on small van.	Mancini Ref. #5 28-29	Yes
		Experiments involving the measurement of voltage buildup on rubber tires. Discusses non-static tires.	Bulgin Ref. #46 583-587	No
	Closed connections cannot yield sparks irrespective of whether conducting or nonconducting hose is used.	Investigates effect of insulated ball valve on flow of toluene/water mixtures in metal pipeline. Electrification increases markedly at constrictions when there is free water present in fluid.	Gibson & Lloyd Ref. #69 339-349	No
		Discusses isolated conductors. Provides example of insulated fittings in GRP tanks.	Gibson & Harper Ref. #11 33-35	No
		Details of experiment involving insulated fittings in GRP tanks.	Tinson Ref. #7 309	No

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.4.1	(continued)	Details of accident case involving leading flange connection.	Luttgens Ref. #7 250-251	No
	Asphalt and crude oils do not have static accumulating capabilities.	Conducted ignition experiments with diesel oil in insulated container. Found there was incendivity to local vapors and oil mist. Also provides theoretical approach.	Britton & Williams Ref. #2 185-206	Needs clarification.
2.4.2	Bond wires not needed around flexible, swivel, or sliding joints.	No information		
	Electrical continuity in fill pipe assembly not needed for closed system loading, and bottom or top loading through tight connections.	No information.		
2.4.3	In past, maximum loading velocity restricted to 15-20 ft/s in tank truck filling.	No information		
	Bulk loading is better criterion than linear velocity for determining electrostatic accumulation.	Discusses variables affecting charge on fuel.	Leonard Ref. #14 17-27	
	Use a vd value of 0.5 maximum for tank trucks: restrict linear flow velocity to 7 m/s maximum.	Discusses new theoretical and experimental studies regarding electrification during tank filling of hydrocarbons.	Macksimov Ref. #10 137-142	No

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.4.3	(continued)	Discusses experimental study performed to determine typical sparking conditions in road tankers. Review studies done by other workers and discusses pros and cons of currently accepted velocity restrictions. Offers recommendations.	Rees Ref. #15 13-25	Yes and No
		Details experiments: proposes velocity restrictions based on these experiments.	Strawson & Lyle Ref. #20 26-30	Yes
		Laboratory and full-scale tests on the loading of iso-octane and jet fuel after passage through a filter. Develops charge relaxation theory.	Bustin Ref. #30 209-216	No
2.4.4	Splash loading may contribute to electrostatic charge generation; during top loading of tank.	Discusses studies concerning drop tube loading of tank trucks and effect of antistatic additives on fuel electrification.	Mahley Ref. #36 53-55	Yes
		Conducted full scale experiments on loading of kerosene into a metal tank. Observed level of sparking in presence of propane air mixture purposely introduced into tank.	Kramer Ref. #19 361-371	Yes
		Survey of studies done by various workers regarding tank truck loading. Briefly presents workers' conclusions.	Leonard Ref. #14 17-22	Yes
		Review of experiments on tank truck loading with low conductivity fuel.	Lyle & Strawson Ref. #35 455	Yes

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.4.4	(continued)	Details of experiments on simulated filling of tank truck with gasolines from different companies. Measured magnitude of charges.	MacKeown & Wouk Ref #35 455	Yes
		Performed experiments to simulate sparking during loading of road tankers. Developed mathematical model of same and compared to experimental results. Offers recommendations for safe filling rates.	Strawson & Lyle Ref. #48 276-287	Yes
		Tests conducted at full-scale fueling test facility to study flow rate, splash loading, temperature, filtration, drop tube vs. bottom loading, and conductivity additives. Additives are recommended as only viable means of static control.	Warren Ref. #50 111-122	Yes
		Tests conducted at full-scale refueling facility to measure charge density on diesel fuel. Provides theoretical treatment of subject. Discusses additives.	Bright Ref. #17 132-139	Yes
		Full-scale experiments that simulate refueler loading. Studied effects of drop tube design, linear velocity, compartment size, fill pipe height, fuel conductivity, wet fuel & filtration.	Mahley & Warren Ref. #58 116-120	Yes
		Experiments with drop tube height; photographs of sparks & turbulence.	Lyle & Strawson Ref. #16 234-247	Yes

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.4.4 (continued)	If fill pipe does not reach tank bottom, restrict flow velocity to 1 m/s until outlet is submerged.	Keep flow rate down until filling pipe is covered.	Tinson Ref. #6 310	Yes
		Critical stage is before fill pipe is submerged; pump at initial rate of 1 m/s.	Bright Ref. #17 138-139	Yes
2.4.5	Bottom loading of tank trucks reduces electrostatic hazards that may arise from improper bonding and positioning of fill pipe	Full-scale experiments on bottom loading of tank refueler with jet fuel. Variables studied were hose diameter & length, & effectiveness of relaxation chamber. Surface potentials obtained in this study are smaller than for top-loading studies. Flow velocity should be well below 30 ft/sec.	Leonard & Carhart Ref. #61	Yes
	Bottom loading produces higher liquid surface voltages than fill pipe loading.	No information.		
2.4.6	History of accidents in unbaffled tank trucks during highway transport due to static generated by splashing of liquid.	Static electricity caused by splashing truck swaying, and rapid movement of truck.	Guest Ref. #18 69	Yes and No
2.4.7	Do not lower conductive objects into tank truck compartment during or immediately after filling; one minute waiting period is sufficient to relax charge.	No information.		
2.5.1	Resistance of rail tank cars to ground through rails is low enough to prevent electrostatic accumulations bonding of tank car or rails to fill pipe is unnecessary.	No information.		

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMENDATION SUBSTANTIATED
2.5.3	For products loaded into railcars with conductivities less than 50 pS/m, restrict vd value to 0.8 and loading velocity to 7 m/s maximum.	Discusses new theoretical and experimental studies regarding electrification during tank filling with hydrocarbons.	Macksimov Ref. #10 137-142	No. Derived a relationship to determine the permissible filling rate based on conductivity, filling pipe size and tank configuration.
		Conducted full scale experiments on loading of kerosene into a metal tank. Observed level of sparking in presence of propane-air mixture purposely introduced into tank.	Kramer Ref. #19 361-371	Yes
		Experiments with drop tube height. Photographs of sparks and turbulence.	Lyle & Strawson Ref. #16 234-247	Yes and No
		Tests conducted at full-scale refueling facility to measure charge density on diesel fuel. Provides theoretical treatment of subject. Discusses additives.	Bright Ref. #17 132-139	No
		Performed experiments to simulate loading of rail tank cars. Developed mathematical model of same and compared experimental results. Offers recommendations for safe filling rates.	Strawson & Lyle Ref. #48 276-287	No. Conducted experiments and developed mathematical model to predict safe filling rates based on type of fluid, pipe diameter and geometry of tank.

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.5.3	(continued)	Full-scale experiments that simulate refueler loading. Studied effects of drop-tube design, linear velocity, compartment size, fill pipe height, fuel conductivity, wet fuel and filtration.	Mahley & Warren Ref. #58 116-120	Yes and No
		Provides details of experiments & reasoning for the given equations.	Stawson & Lyle Ref. #20 26-30	Yes
2.5.4	Unloading procedures of any type for rail tank cars need no protective bonding.	No information.		
2.6	Metal drums and cans being filled from other containers while both rest on conductive foundations need no further bonding as long as the fill nozzle remains in contact at metallic spout.	Presents details of experiments simulating worst case scenario for unlined drum filling. Also presents theoretical models.	Britton & Smith Ref. #21 65-72	Yes
2.7	Bonding or grounding of cars while being filled at gas station is unnecessary.	Conducted experiments; sample calculation showing hypothetical case; need more than 100,000 megohms in tires to charge car.	MacKeown & Wouk Ref. #22 661-664	Yes
	Bonding between tank trucks and underground gas stations tanks is unnecessary, provided that hose nozzle remains in metallic contact with tank fill pipe or is tightly connected.	Details of experiment; total charge produced in this case showed up to be much less than filling truck at the filling rack.	MacKeown & Wouk Ref. #22 661, 663	Yes
2.8	Protection against electrostatic discharge is achieved for filling marine craft if fueling nozzle is kept in metallic contact with fuel tank fill pipe.			Yes and No

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.9	Regarding aircraft fueling:			
	a) Bond fuel hose nozzle to plane by means of short bond wire and clip.	Survey of studies done by various workers regarding aircraft fueling. Briefly presents workers' conclusions.	Leonard Ref. #14 17-22	RP 2003 does not address aircraft fueling in much detail.
		Conducted laboratory scale experiments involving filter & tank arrangement for circulation of fuel. Simulation of spark discharges during aircraft fueling.	Leonard Ref. #42 100-111	Same
		Review of studies on aircraft fueling.	Lyle & Strawson Ref. #35 455	Same
		Presents simulated aircraft fueling experiments to show how fuel conductivity varies during loading procedure.	Foster Ref. #44 78-88	Same
		Laboratory and full-scale tests on the loading of jet fuel after passage through a filter. Develops charge relaxation theory.	Bustin Ref. #30 209-216	Same
		Developed theoretical model of rectangular metal tank partially filled with charged liquid. Calculated ES potential, field and energy. Compared results to actual aircraft fueling experiments. Found reasonable agreement between calculated and experimental values.	Carruthers & Wighley Ref. #77 180-195	Same

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.9	(continued)	Bond nozzle to aircraft to avoid unknown or unanticipated problems; other bonding is designed to control external sparks which have a low probability of occurring. No universal consensus otherwise. Requires further investigation.	Mancini Ref. #5 29	Yes and No
	b) If small planes are fueled by gas station type hose (up to 25 gal/min), bonding is not necessary.	No information.		
	c) Some laws require plane, fueler, and hydrant vehicle to be interconnected by bond wires to low resistance ground (less than 10,000 ohms).	Simulated large-scale experiments of fueling justify potential hazards and the need for investigating means of static control.	Bruinzeel Ref. #24 125-139	No
	d) No bonding required when fueling aircraft through a tight metal-to-metal connection.	Simulates experiments with aircraft hoses; verifies external bonding wire clip arrangement as best.	Carruthers Ref. #25 176-177	Yes
2.10	Regarding tank ship/barge loading:			
	a) Limit velocity of incoming liquid to 1 m/s until inlet opening is submerged from 0.3 to 2 meters.	Discusses conclusions drawn from early study done on tanker loading.	Mahley Ref. #36 55	No
		Review of work on ship tank loading related to liquid charge density.	Lyle & Strawson Ref. #35 454	No, Theoretical & experimental measurements of charge density in ship tank loading. No generalization & results.

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.10	(continued)	Computer modeling of ignition hazards arising during the loading of tankers with hydrocarbon products. Focuses on sparks arising from fixed-in-place tank washing equipment. Suggests spark-relieving techniques.	Butterworth & Brown Ref. #47 9-26	No. Published experimental results on electrostatic conditions in tank washing machine.
	b) Use inert gas blanketing or conductive additives as an alternative.	Inert gas is often effective in fuel handling but costly and difficult to maintain.	Smith Ref. #59 64	Yes and No
	c) No bonding required because hull of ship is in contact with water and is inherently grounded.	Details accident case involving the loading of kerosene into a steel barge.	Beach Ref. #9 85-86	No
		Bonding serves no useful purpose in any kind of water, even if the hull is painted or covered with marine growth.	Mancini Ref #5 29	Yes
2.11	Regarding metal storage tanks:			
	a) Static generating and static-dissipating qualities of stored liquid determine possibility of sparking.	Accident case history involving the filling of a tank with liquid diphenyl. A layer of solid diphenyl subsequently formed on inside surface of vessel, preventing dissipation of charge.	Luttgens Ref. #7 251-253	Yes
	b) Avoid splash filling; outlet of fill pipe should discharge near bottom with minimum agitation.	Discusses example of acid transfer by compressed air into tank. Provides calculations.	Saletan Ref. #4 104-105	Yes
		Details of accident case involving insulated rubber sleeve on metal funnel used to fill metal storage tank.	Loveland Ref. #27 5	Bonding is not addressed for storage tanks.

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMENDATION SUBSTANTIATED
2.11	(continued)	Review of work on large storage tank.	Lyle & Strawson Ref. #35 455	Yes
	c) Limit velocity of incoming liquid to 1 m/s until outlet is well submerged.	Conducted experimental studies to determine safe filling rates after rail and food tank cars.	Stawson Ref. #12 16	No
	d) In the case of a floating-roof tank, follow above precautions until roof becomes buoyant; no precautions necessary after this because of the absence of a flammable vapor space.	Discusses experimental study involving the use of floating blankets of different designs.	Mahey Ref. #36 52	The topic of floating blankets on liquid surface of cone roof tanks is not addressed.
	e) Some types of nonconducting floating-roof tank covers have isolated metallic clips which require bonding.	No information.		
2.12	Regarding air-blown agitators:			
	a) Causes prolific electrostatic discharge.	No information.		
	b) Protect agitator vessel by inert-gas blanketing or by continuous treating system.	No information.		
2.13	Regarding blending tanks and mixers:			
	a) In-tank jet mixing and high velocity propeller mixing stir up settled water and generate electrostatic charge.	Details of recurring accident cases involving the blending of silicone products.	Beach Ref. #9 86-87	Yes
		Details of experiments involving measurements of charge density during mixing in a small vessel with nonconductive solvents.	Owens Ref. #34 734-748	Yes

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMENDATION SUBSTANTIATED
2.13	(continued)	Discusses mixing vessels and their hazards. Provides accident case histories and safety recommendations.	Owens Ref. #56 1428-1429	Yes
		For high energy mixing & blending operations, a "safe figure" of about 1000 pS/m has been suggested.	Loveland Ref. #27 9	No
	b) Floating roof tanks are desirable for blending or if necessary, use gas blanketing.	Inert atmosphere is often effective in fuel handling but costly and difficult to maintain.	Smith Ref. #59 64	Yes and No
2.14	Coating of paint, plastic, or aluminum oxide on inside of cargo or storage tank does not present electrostatic hazard.	Gives details of ignition experiments performed on plastic sheets and plastic coated metal surfaces.	Heidelberg Ref. #37 147-155	Yes, although RP 2003 does not discuss coating thickness.
		Presents theoretical and experimental discussion of lined drums.	Britton & Smith Ref. #21 70, 72, 77-78	Yes
		Measurements of electrostatic charging capacity of various films and coatings with different thicknesses. Thin porous coatings do not cause brush discharges but nonporous thin coatings can.	Maurer Ref. #85 217-222	Yes
2.15	Regarding sampling, gauging, high level devices:			
	a) Use natural fiber ropes, not synthetic ropes.	No information.		
	b) Wait 30 minutes after filling large storage or ships' tank before hand gauging or sampling.	No information.		

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.15 (continued)	c) In tank trucks, rail cars or smaller volume vessels, wait 1 minute more before gauging or sampling.	Experiments on initiation of sparking with metal electrodes lowered to kerosene surface after flow of kerosene through a filter to a large tank.	Johnson Ref. #70 53-65	Yes
	d) Completely nonconductive hand gauging or sampling devices require no waiting period.	No information.		
	e) Bond floats of automatic gauging devices to vessel shell through lead-in tapes and/or guide wires.	No information.		
	f) Fires caused by static electricity during LP-gas sampling rarely occur; fires confined to open sample containers.	No information.		
	g) Open metal graduates used for sampling must be bonded to fill pipe.	No information.		
	h) If graduate is nonconducting or if a closed container sampling procedure is used, bonding or grounding is not useful.	No information.		
	i) Alarms or detectors used in the presence of flammable vapor-air mixtures should be made of nonconductive material or be properly bonded.	No information.		
2.16	Regarding abrasive blasting:			
	a) Sparks have been observed jumping from rubber hose to grounded objects during grit blasting.	Experiments on solid particles issuing as a jet through an orifice. Nature of charge acquired is investigated.	Banerji Ref. #53 428-431	Yes

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.16 (continued)	b) Special hoses with built-in metallic shielding to prevent sparking are available from vendors.	No information.		
	c) Within stream pattern no flammable concentration likely to exist because of sweeping action of air stream.	No information.		
2.17	Regarding purging & cleaning of tanks and vessels:			
	a) Steam jets generate prolific charge on nozzle and insulated objects on which the steam impinges.	Discusses 1969 tanker explosions that occurred during washing.	Mahley Ref. #36 55-57	Yes
		Details experiments involving the measurement of static charge and field strength produced by steam jets and water atomizer.	Napier Ref. #39 244-265	Yes
		Brief discussion on previous work regarding water jets.	Klinkenberg Ref. #29 65-66	Yes
		Discusses common situation of tank cleaning with an organic solvent flowing through spray nozzle. Provides calculations.	Saletan Ref. #4 103-104	Yes
		Discussion of charge generation during tank washing.	Van Der Meer Ref. #49 153-156	Yes

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.17	(continued)	Experiments on full-scale tanks to simulate charged mist generation during tank washing. Insulated objects inside tank were charged rapidly and ignitable sparks were observed.	Van Der Weerd Ref. #50 158-177	Yes
		Experiments on liquid sprays, liquid jets and gas jets. Discussion on how charge develops in each of these situations.	Banerji Ref. #53 409-428, 431-433	Yes
		Laboratory-scale tests to simulate tank washing operations. Emphasis on earthed protrusions in a charged water aerosol and the presence of isolated slugs of water.	Hughes Ref. #60 966-971	Yes
		Laboratory-scale experiments on charges produced on mists by jets. Current generation dependent on jet velocity and liquid conductivity.	Vos Ref. #65 184-192	Yes
		Laboratory-scale experiments of test effect of organic additives and strong electrolytes on charging of water mist. Seawater-crude oil mixtures also tested. Level of charge depends on type and concentration of solute and water-oil ratio.	Vos Ref. #66 165-171	Yes

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.17	(continued)	Full-scale tests on tanks equipped to produce charged mists. Spark mechanism associated with water slugs. Ignition tests associated with protruding objects inside tank.	Van De Weerd Ref. #67 295-309	Yes
		Theoretical approach to charge generation during tank washing. Four different geometric configurations developed.	Smit Ref. #68 178-183	Yes
		Experiments on spraying of kerosene-water mixtures. Charge density markedly increased in the presence of free water. See Figure 7.	Gibson Ref. #72 80-81	Yes
		Brief discussion on electrification of drops and sprays. Sample calculation.	Cooper Ref. #73 513-514	Yes
		Computer modeling of tank washing operations and associated ignition hazards. Focuses on isolated slugs of wash water.	Chubb Ref. #74 71-87	Yes
		Computer studies on isolated slugs of wash water and on sloshing of liquid contents as pertains to ESD hazard in tanker operations. Shore tank studies of simulated washing showed low-energy sparks when jets were directed either straight up or straight down.	Chubb Ref. #75 61-70	Yes
		Comparison of small scale studies with full-scale washing operations. Review of studies on aerosol generation.	Bright Ref. #76 37-44	Yes

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMENDATION SUBSTANTIATED
2.17 (continued)	b) All conductive insulated objects subject to impingement or condensation, including discharging pipe should be bonded to tank or equipment, or be grounded.	No information.		
	Regarding the use of CO_2 in tanks & vessels:			
	a) Jet of CO_2 generates static due to CO_2 snow.	Discusses experiment done with CO_2 issuing from a cylinder of liquid carbon dioxide. Magnitude of charge on CO_2 related to pressure in cylinder and friction associated with impingement on surface.	Banerji Ref. #53 431-433	Yes
	b) Putting CO_2 in vessel form of dry ice & allowing to vaporize is acceptable.	No information.		
	c) CO_2 extinguishers should not be used for inerting.	Release of CO_2 at high velocity produces electrostatic and incendive discharges. Do not use CO_2 for inerting.	Butterworth Ref. #26 161-169	Yes
		Suggests design for antistatic CO_2 nozzle.		
2.18	Regarding belts:			
	a) If pulley is made from conducting material, charge will be dissipated through shaft & bearing.	Provides sample calculation of a pulley attached to a machine insulated from earth.	Strawson Ref. #12 15	Yes

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMENDATION SUBSTANTIATED
2.18 (continued)	b) Use belt made of conductive material or apply conductive dressing.	Develops mathematical model of moving sheet material on grounded conducting roller. Simulates insulator belts. Charging depends on conductivity and speed of sheet.	Horvath & Berta Ref. #32 259-263	
		Experiments on an insulating belt slipping on metal roller. Shows that charge density exponentially approaches a limiting value as work done against friction is increased.	Cunningham Ref. #80 1734-1736	Yes
		Measurements of potentials generated on belts of rubber, neoprene, PVC & polyethylene running over metal rollers as a function of speed. Charge generation mainly influenced by surface resistivity.	Javadi & Napier Ref. #87 266-279	Yes
	c) Avoid use of flat belts in hazardous areas; V-belts are acceptable.	No information.		
2.19	Regarding filters & relaxation chambers:			
	a) A liquid of low conductivity will accumulate static charge when pumped through a pipe; charge will dissipate when a voltage builds up.	Discusses study done on polyethylene pipe carrying kerosene to determine level of discharges from pipe surface.	Mason Ref. #38 137-144	No. RP 2300 does not address plastic piping.
		Conducted experiments involving flow of heptane through PVC tubing to measure liquid charge and tubing charge.	Keller Ref. #40 1433-1438	No. RP 2300 does not address plastic piping.

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.19	(continued)	Survey of studies done by various workers regarding flow of hydrocarbons through nonconducting tubing. Briefly presents workers' conclusions.	Leonard Ref. #14 23-27	No. RP 2300 does not address plastic piping.
		Measurements of charge density developed on polyethylene pipe by liquid flow.High resistivity liquids show virtually no charge decay. See Figure 6.	Gibson Ref. #72 79	RP 2300 does not address plastic piping.
		Review of charge relaxation theory & summaries of studies by other workers.	Cooper Ref. #73 512-515	Yes
		Theoretical predictions & supporting work in laboratory regarding hydrocarbon flow in conducting & nonconducting pipes. Studied iso-octane in metal container with filter arrangement.	Carruthers Ref. #25 169	Yes and No
		Studied current generated in toluene flowing in large scale SS pipe-line system. Electric current dependent on flow velocity, pipe diameter & pipe length. Purpose of study is to help develop equations that can predict current generation for large scale systems.	Gibson & Lloyd Ref. #62 89-99	Studies on current generation in flow not addressed in detail in RP 2003.
		Charge relaxation is of hyperbolic form.	Bustin Ref. #30 210	Yes
		Charge density achieves a steady state value after a certain pipe length.	Britton & Smith Ref. #1 55-56	Yes

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMENDATION SUBSTANTIATED
2.19 (continued)	b) Presence of a filter can produce 10-200 times more charge in a system; no danger as long as liquid is kept in pipe.	Study conducted to observe relationship between chemical nature of fuel additives and charging tendency by passage through filters.	Leonard Ref. #14 28	Yes and No
		After passage through a filter, charge density of liquid increases 1-3 orders of magnitude. Suggestions for relaxation chambers.	Britton & Smith Ref. #1 55-56	Yes
		Not possible to predict effect of filter due to various types of construction.	Strawson Ref. #12 13	No
		Discusses charge relaxation downstream of a filter.	Britton & Smith Ref. #21 73	Yes
		Laboratory and full-scale tests on the loading of iso-octane and jet fuel after passage through a filter. Develops charge relaxation theory.	Bustin Ref. 330 209-216	Yes
	c) At least 30 seconds of relaxation time between filter and discharge point is necessary.	Comparison of relaxation criteria given by various codes.	Britton & Smith Ref. #21 71	No
		Relaxation time 2.	Eichel Ref. #13 166	In some cases.
		30 seconds is adequate for fuels regardless of conductivity.	Leonard Ref. #14 20	Yes
		Both 30 second constraint and 3 constraint can yield practical difficulties.	Britton & Smith Ref. #1 63, 55-56	Yes and No

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.19 (continued)	d) Relaxation time provided by sufficient piping volume.	No information.	Loveland Ref. #27 9	No
	e) Ignore relaxation criteria for liquids with conductivities 50 pS/m.	For general transfer operations, there is no ESD hazard if conductivity of liquid is 100 pS/m.	Mancini Ref. #5 24	Yes, but does not distinguish between insulated and noninsulated piping.
		Static charge accumulation is usually not significant for liquids with conductivities 50 pS/m, providing that liquid is handled in grounded metal equipment (with the exception of mists). Results of experiments verify that 50 pS/m is a safe value.	Britton & Smith Ref. #121 71	Yes
2.20.1	Buried plastic tanks are not an electrostatic discharge problem.	Buried plastic tanks can be used if made of conducting polymeric material or if electrostatic build-up is controlled in system including earthed metal attachments.	Gibson & Harper Ref. #11 38-39	No
2.20.2	Test sample of aboveground glass-reinforced plastic tank showed it had a conductivity 100 times great as typical liquid product being handled.	Details accident cases involving ignition in a plastic drum and ignition in a ceramic-lined ball mill.	Loveland Ref. #27 8	Yes, Addresses high levels of charge found having insulated properties.
		Discusses the use of plastic containers & provides accident case study on fiberglass reinforced plastic tank.	Mancini Ref. #5 29-30	Yes, Addresses containers having insulating properties.
		Conducted experiments involving flow of charged diesel into GRP tank. System also modeled on computer.	Lees Ref. #41 267-273	Yes

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.20.2	(continued)	Survey of studies done by various workers regarding GRP tanks. Briefly preworkers' compensation.	Leonard Ref. #14 23-27	Yes
		Review of work on filling of plastic tanks with fuel.	Lyle & Strawson Ref. #35 456	Yes
		Computer modeling of flow of hydrocarbons into plastic storage tank. Attempt to predict electric field and potential for general applications.	Diserens Ref. #43 169-181	Yes
		Most investigations indicate that the charge density of a polymeric material can, under certain conditions, become high enough to cause discharge. Uses polyethylene tubing & sheets as examples.	Gibson & Harper Ref. #11 28-33	Yes
		Due to wear and ultraviolet exposure, plastic surfaces become hydrophilic. Together with water and dirt they produce areas of high surface conductivity. These can migrate to metallic areas.	Rosenthal Ref. #31 51-52	Yes
	In tests involving pumping fuel into an insulated plastic tank, metallic fittings showed accumulated potentials of up to 11 kV.	Discusses isolated conductors & appropriate earthing & bonding procedures where nonconducting materials may be used.	Gibson & Harper Ref. #11 33-37	Yes

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.20.2	(continued)	Discusses series of experiments performed to show that brush discharges from plastic surfaces can ignite certain gases and vapors.	Glor Ref. #45 327-332	Yes
		Experiments on GRP storage tank and GRP road tanker that simulate loading of fuel. Charge of up to 11 kV observed on insulated metal connections. Recommend proper electrical bonding to reduce hazards.	Tinson Ref. #6 303-311	Yes
		Experiments involving GRP tanks, plastic pipes & rubber nozzles. Discusses charge density & surface potential.	Bright Ref. #17 139-144	Yes
		Series of experiments performed to show that brush discharges can occur from PVC plates charged by induction. Also discusses method for estimation of critical charge density for ignition.	Lovstrand Ref. #79 161-168	Yes
		General discussion of work on ESD from nonconducting surfaces. Experiments on rubbing of polyethylene sheets and tubing, and probability of ignition.	Gibson & Harper Ref. #86 27-35	Yes

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMENDATION SUBSTANTIATED
2.20.2 (continued)	Test sample of insulated plastic tank with metallic fittings showed accumulated potentials of up to 11 kV.	Proper electrical bonding makes insulated tanks with conductive fittings sufficiently conductive. Tests showed accumulated potentials of up to 11 kV for insulated plastic tanks.	Tinson Ref. #6 303-311	Yes
	Bond together and ground all external metallic objects contacting outside of aboveground plastic tank.	Charge seen on objects not directly in contact with tank.	Tinson Ref. #6 309	Yes
2.20.3	Bond only the metal parts on a plastic container to fill pipe.	Details accident cases involving charged plastic sack & polycarbonate handlamp.	Loveland Ref. 327 7	Other uses of insulating surfaces in a flammable atmosphere are not addressed in RP 2003.
		Discusses plastic containers. Provides sample calculation & accident case history.	Owens Ref. #56 1427-1428	No
		Accident case history involving induction charging on plastic bottle. Provides sample calculation. Offers safety guidelines.	Owens Ref. #64 37-38	No
		Accident case history involving the drainage of ethylenoxide into a plastic bucket.	Luttgens Ref. #7 249-250	No
		Conductive liquid bridging forms a conduction path back to the grounded effective filling system and is effective. Volume resistivity of the product handled is of primary importance in charge dissipation & relaxation.	Rosenthal Ref. 31 51	

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.20.4	Avoid sheet plastic for lining drums; lab tests show incendiary sparks.	Presents analytical solutions of Poisson's equation regarding charge relaxation in a vessel lined with insulating dielectric layer.	Jones Ref. #28 199-211	Yes
		Discusses plastic lined containers. Provides sample calculation & accident history.	Owens Ref. #56 1427-1428	Yes
		Accident case histories involving plastic liners. Offers safety recommendations.	Owens Ref. #64 38	Yes
		Test setup to observe spark discharges on plastic film when approached by metal electrode. Estimated discharge energy & calculated potential for ignition. Compared calculated value to actual ignition experiments.	Tabata & Masuda Ref. #82 1206-1210	Yes
		Tests conducted on polyethylene sheets to study characteristics of charge generated by rubbing ability of discharges to ignite coal gas, methane & solvent-air mixtures. Concludes that ignition could occur under certain environmental conditions.	Gibson & Lloyd Ref. #84 1619-1631	Yes
		Measurements of electrostatic charging capacity of various films and coatings with different thicknesses. In general, porous materials & thin porous coating do not cause brush discharges. Packaging materials & nonporous materials do.	Maurer Ref. #85 217-222	Yes

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMENDATION SUBSTANTIATED
2.20.4	(continued)	Experiments on plastic film, synthetic cloth and silicon oil to measure ES discharges by approaching metal sphere. Ignition observed with plastic film.	Tabata Ref. #89 50-56	Yes
		Sample calculation involving nonconducting liner. Increasing use makes them worthy of consideration.	Saletan Ref. #4 105	Yes
2.20.5	Static ignition of petroleum vapors by wearing apparel constitutes low hazard; not necessary to ground personnel or provide antistatic clothing.	Charged personnel can ignite flammable atmosphere, discusses ways in which personnel can become charged. Recommend antistatic footwear and noninsulating floors. Details of accident case involving paint spraying gun.	Loveland Ref. #27 3-6	No
		Details of experiments involving ignition of an acetone/ air mixture by simulation of human spark scenario. Suggests that vapor/air mixtures of 5 mJ or less can be ignited by human sparks and that precautions need to be taken.	Johnson Ref. #23 29-34	No
		In case of thick layers used for protection against corrosion, electrostatic discharge should be considered a hazard; also gives details of ignition experiments performed on plastic sheets and plastic-coated metal surfaces.	Heidelberg Ref. #37 147-155	Yes

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.20.5	(continued)	Experimental work on ignition of natural gas/air mixtures by human-induced sparks. Studied nature of spark behavior.	Wilson Ref. #52 21-27	No
		Experimental work with stored charge energy on body as related to various clothing materials. Recommends low resistivity clothing & antistatic footwear.	Wilson Ref. #33 67-84	No
		Experiments on clothing of different materials to determine if accumulated charge is high enough to ignite gas/air mixtures. Also measured resistivity of clothing & typical body voltage.	Henry Ref. #54 212-225	No
		Discusses static electricity & work- clothing. Covers effects of relative humidity & antistatic treatments.	Verschave Ref. #55 287-289	No
		Discusses clothing & personnel electrification. Offers methods of achieving antistatic behavior in garments. Recommends proper grounding of personnel.	Owens Ref. #56 1424-1427	No
		Brief summaries for several articles concerning human spark ignition experiments.	Berkey Ref. #57 32-36	No

SUMMARY OF LITERATURE SUPPORT FOR RP 2003

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT LITERATURE SAYS	LIT REF	IS RP 2003 RECOMMEN-DATION SUB-STANTIATED
2.20.5	(continued)	Experiments on cotton & polyester to determine accumulated charge after rubbing with nylon and Teflon. Ignition tests with natural gas/air mixtures were also conducted. Brush discharges are readily produced. Some incendiary behavior noted.	Wilson Ref. #63 231-245	Yes and No
		Measured charge accumulated on different types of clothing material by contact and means. Showed that many synthetic materials should be avoided in flammable atmospheres.	Hammant Ref. #78 343-350	No
		Conducted rubbing tests on polyacrylate, cotton, polyester, & polyester/cotton blends. Samples rubbed with similar materials. Good reproductibility observed among data. Cotton showed high charging tendency.	Heidelberg Ref. #81 305-308	No
		Conducted rubbing tests on a variety of woven cloths to measure generated charge density. Good reproductibility among data. Separation charges & approaching discharges also studied.	Hirakawa Ref. #83 269-276	No
		General discussion of electrostatic problems presented by personnel. Review of studies by various workers.	Brundrett Ref. #88 295-312	No

APPENDIX B

STANDARDS COMPARISON

COMPARISON OF RP 2300 WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.1	Resistances of less than 1 meg-ohm may act as short circuits.	No information.		
2.31 - 2.33	Figure 1 shows relationship between temperature, vapor pressure, flammability limits of petroleum products.	Graph 1 shows same relationship between temperature, vapor pressure and flammable limits of petroleum products conditions are optimum for ignition midway between upper and lower flammable limits.	NFPA 77 Ref. #1 77-24 to 77-25	Yes
		Figure 2 shows plot of ignition energy versus % flammable material in air; minimum ignition energy is best measure for determining explosion and fire hazards.	British Standards Institute Ref. #4 Sect.7.2	
2.4.1	Regarding tank trucks:			
	a) Bond wire connection is essential where high- and intermediate vapor pressure products are loaded through top domes.	Binding facilities for protection during loading of tank vehicles through open domes are required for Class I liquids or switch loading of Class II/Class III liquids.	NFPA 30 Ref. #1 30-36	Yes
		Open-dome loading of tank trucks offers significant static hazard at rates above 100 GPM. Bond should be established between loading piping and tank; switch loading of low vapor pressure products can be static hazard.	NFPA 77 Ref. #2 77-32 to 77-35	Yes
		Sparking can occur in open-dome filling of tank trucks; bond tank to fill pipe before filling starts and until filling is complete.	Fire Protection Handbook Ref. #3 5-36	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.4.1	(continued)	Before making pipe connections or opening dome lid, tank should be bonded to appropriate earth point and should remain in position throughout filling.	British Standards Institute Ref. #5 Sect.9.3.1	Yes
	b) Bond resistance as high as 1 megohm is adequate for static dissipation.	Ground resistance of 1 megohm is adequate for static grounding because leakage currents are extremely small.	NFPA 77 Ref. #2 77-16	Yes
		Usually any resistance path of less than 1 megohm will serve.	Fire Protection Handbook Ref. #3 5-34, 5-37	Yes
		Resistance to earth of transportable metal items should be kept below 10 ohms.	British Standards Institute Ref. #4	No
		All conductive parts of equipment shall be grounded so that resistance does not exceed 25 ohms.	Army Safety Manual Ref. #6 7-1	No
		Nearly any conductor up to 1,000,000 ohms resistance will be satisfactory.	National Safety Council Ref. #7 2	Yes
	c) Asphalt and crude oils do not have static accumulating capabilities.	Asphalts (including cutback asphalts), most crude oils, residual oils, and water-soluble liquids do not have a static accumulating tendency.	NFPA 30 Ref. #1 30-36	Yes
		Bonding not required when loading products not having static generating abilities such as asphalt and crude oil.	NFPA 77 Ref. #1 77-34	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.4.1	(continued)	If a liquid has a conductivity greater than 50 pS/m, it is incapable of retaining a hazardous charge; alcohols, ketones, black petroleum oils, and crude oils are in this category.	British Standards Institute Ref. #4 Sect. 9.2.2	Yes & No
	d) Closed connections cannot yield sparks irrespective of whether conducting hose is used.	Bonding is not required where vehicles are loaded through closed-bottom or closed-top connections whether hose or pipe is conductive or nonconductive.	NFPA 30 Ref. #1 30-36	Yes
		Bonding is not required where vehicles are loaded through closed connections, irrespective of whether the hose or pipe used is conducting or nonconducting.	NFPA 77 Ref. #2 77-34	Yes
		Discusses the presence of nonconducting components that could cause insulation of metallic components.	British Standards Institute Ref. #4 Sect. 14.3.2	Nonconducting materials may cause insulation of metallic components.
		1. Ignition risks may be encouraged when hose connections are made or broken, due to sparking from stray currents flowing in hose string. 2. Nonconductive hose may become charged and if two or more hoses are joined by metallic flanges, the flanges can spark. 3. Advises routine electrical continuity checks because maintenance or modification could affect continuity.	British Standards Institute Ref. #5 Sects. 9.1, 9.2	No

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.4.1	(continued)	Bonding is not needed for metallic connections; only for non-insulated parts.	Handbook of Industrial Loss Prevention Ref. #9 30-7	Yes & No
		Sparking when manipulating hose fittings, ball valves.	Swiss Chemical Industry Ref. #8 3	No
2.4.2	Regarding tank trucks:			
	a) Bond wires are not needed around flexible, swivel, or sliding joints because metallic fill pipe assembly forms a continuous electrically conductive path.	Bonding not needed around flexible metallic piping or metallic swing joints but bond should be provided around joints made of non-metallic insulating material.	NFPA 77 Ref. #2 77-31	Yes
		Swivel joints in stand pipes and metal loading arms should be electrically continuous. Advises routine continuity checks before equipment is brought into use.	British Standards Institute Ref. #5 Sect. 9.2.1	Yes & No
	b) Electrical continuity in fill pipe assembly not needed for closed system loading (such as LP-gas loading).	Bonding is not required where vehicles are loaded through closed-bottom or closed-top connections whether the hose or pipe is conductive or nonconductive.	NFPA 30 Ref. #1 30-36	Yes
		Bonding is not required where vehicles are loaded through closed connections, irrespective of whether the hose or pipe used is conducting or nonconducting.	NFPA 77 Ref. #2 77-34	Yes
		Bonding is not required when LP-gas vehicles are loaded or unloaded through closed connections.	Fire Protection Handbook Ref. #3 5-37	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.4.2	(continued)	Discusses the presence of nonconducting components that could cause insulation of metallic components.	British Standards Institute Ref. #4 Sect. 14.3.2	No
		Liquified petroleum gas road tankers should be earthed during both loading and discharging by being bonded to a suitable earth point.	British Standards Institute Ref. #5 Sect. 9.3.3 See also Sect. 9.1, 9.2	No
	c) Electrical continuity in fill pipe assembly not needed for bottom or top loading through tight connections.	No information.		
2.4.3	In past, maximum loading velocity restricted to 15-20 ft/s in tank truck filling.	No information.		
	Bulk loading rate is better criterion than linear velocity for determining ES accumulation in tank truck filling.	Total charge carried into vehicle depends on generating characteristics and total quantity of liquid delivered. Rate of generation for a system of any given dimensions is a function of linear flow velocity.	NFPA 77 Ref. #2 77-32	Yes & No
		Velocity restrictions depend on type of material flowing through pipe and pipe size.	Swiss Chemical Industry Ref. #8 3-4	No
	Use a vd value of 0.5 maximum for tank trucks; restrict linear flow velocity to 7 m/s maximum.	During tank filling velocity of incoming liquid may gradually be increased to 15-20 ft/s.	NFPA 77 Ref. #2 77-35	-
		In the light of present knowledge it is undesirable in any case for the pipeline velocity to exceed 7 m/s.	British Standards Institute Ref. #4 Sect. 9.3.2.1	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.4.3	(continued)	Maximum linear flow velocity for top loading may be expressed in terms of velocity V of the liquid flowing in pipe section of diameter d. Velocity V is lower of those given by the expressions V=7 and Vd=0.5	British Standards Institute Ref. #5 Sect. 7.3.3	Yes
		Discusses how produce flow is also governed by other pipe diameter and length guidelines may be exceeded for a particular system if sufficient experience with that system demonstrates that it is safe.	British Standards Institute Ref. #5 Sect. 7.3.3	Yes
2.4.4	Splash loading may contribute to ES charge generation; during top loading, fill pipe should reach close to or touch tank bottom.	Filling through open domes into tanks of tank vehicles shall be by means of a downspout that extends near the bottom of the tank.	NFPA 30 Ref. #1 30-36	Yes
		Fill pipe should reach as close as possible to the bottom of the tank being loaded, and preferably be in contact with the bottom.	NFPA 77 Ref. #2 77-34	Yes
		Splash filling into a tank where a flammable atmosphere may exist should be in order to prevent formation of charged mist. Internal fill pipe should reach bottom of tank or hose or loading arm nozzle should be inserted to bottom without actually touching it.	British Standards Institute Ref. #5 Sect. 7.3.1	Yes
		For open-dome filling, have filling tubes near bottom of tank. Contact fill opening with tube. Discusses turbulence.	Handbook of Industrial Loss Prevention Ref. #9 30-6, 30-7	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.4.4	(continued)	Take filling tube down to bottom to avoid bubbles, eddies and splashing.	Swiss Chemical Industry Ref. #8 4	Yes
		Splashing and impingement on surfaces cause ES charging. Use fill pipe extending to bottom of tank.	British Standards Institute Ref. #4 Sect. 9.3.2.2	Yes
		Generation of charge can occur within a container by splashing or spraying of incoming stream.	Fire Protection Handbook Ref. #3 5-37	Yes
	If fill pipe does not reach tank bottom, restrict flow velocity to 1 m/s (3 ft/s) until outlet is submerged.	If fill pipe does not reach tank bottom, the liquid velocity in the fill pipe should be limited to about 3 ft/s until outlet is submerged.	NFPA 77 Ref. #2 77-34 to 77-35	Yes
		For liquids up to and including 50 pS/m, linear flow velocity in a pipe used for top loading should not exceed 1 m/s if a second immiscible phase is present.	British Standards Institute Ref. #5 Sect. 7.3.3	Yes & No
2.4.5	Bottom loading of tank trucks reduces ES hazards that may arise from improper bonding and positioning of fill pipe.	Splash filling into a tank where a flammable atmosphere may exist should be avoided in order to prevent formation of charged mist. This can be achieved by bottom entry.	British Standards Institute Ref. #5 Sect. 7.3.1	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.4.5 (continued)	Bottom loading rates for tank trucks should comply with the flow restrictions associated with Vd=0.5.	When bottom loading a tank vehicle, a means shall be provided for loading a predetermined quantity along with a secondary automatic shutoff to prevent overfill. The connection between the loading hose/pipe and truck piping shall be a dry disconnect coupling.	NFPA 30 Ref. #1 30-37	NFPA 30 does not apply to static issues here.
		Bottom loading generates higher potentials at liquid surface than top loading because of the absence of earthed fill pipe. Unless a dip tube, standpipe or baffle plate is mounted centrally in the tank, reaching from top to bottom, it is recommended that flow rates for bottom loading be 25% below those for top loading (using the restrictions associated with Vd-0.5).	British Standards Institute Ref. #5 Sect. 7.3.3	Yes
	Bottom loading in tank trucks produces higher liquid surface voltages than fill pipe loading.	Where bottom loading is used, low velocity or splash deflectors should be in place to prevent upward spraying of product and to minimize surface turbulence.	NFPA 77 Ref. #2 77-35	Yes
2.4.6	There have been accidents in unbaffled tank trucks during highway transport due to static generated by splashing of liquid.	No information.		
2.4.7	Do not lower conductive objects into tank truck compartment during or immediately after filling; one minute waiting period is sufficient to relax charge.	Metal or conductive objects (gauge tapes, sample containers, thermometers) should not be lowered into or suspended in tank during or immediately after. Wait about one minute.	NFPA 77 Ref. #2 77-35	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.4.7	(continued)	Risk can be controller by avoiding operations that promote discharge of surface charge. (Delay introducing conductive gauging & sampling devices).	Fire Protection Handbook Ref. #3 5-37	Yes
		Gauging/sampling should not be carried out while any charge generating operation is going on or for at least 30 minutes afterwards (for liquids with conductivities up to and including 50 pS/m & containing a water phase).	British Standards Institute Ref #5 Sec. 6.2, 6.3, 7.5	Yes & No
2.5.1	Resistance of rail tank cards to ground through rails is low enough to prevent ES accumulation; bonding of tank car or rails to fill pipe is unnecessary except when requiring protection against stray currents.	To protect against stray currents, tank car facilities where flammable and combustible liquids are loaded/unloaded through open domes shall be protected by permanently bonding fill pipe to at least one rail and to rack structure (if of metal).	NFPA 30 Ref. #1 30-36	Yes
		Resistance of tank car to ground through the rails, % the resistance of piping, flexible metallic joints or metallic swivel joints are adequately low for static electricity protection.	NFPA 77 Ref. #2	Yes
		Both rails of railway tracks should be bonded permanently to each other and to the earthed pipeline.	British Standards Institute Ref #5 Sect. 9.4.1, 9.4.2, 8.1-8.4.3	Yes & No
		The rail car itself is earthed by contact between its wheels and the rails. Also offers recommendations concerning non-metallic rail tank cars.		

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.5.1	(continued)	No bonding required because resistance is very low.	Handbook of Industrial Loss Prevention Ref #9 30-7	Yes
2.5.3	For products loaded into rail cars with conductivities less than 50 pS/m, restrict vd value to 0.8 and loading velocity to 7 m/s maximum.	No information.		
2.5.4	Unloading procedures of any type for rail tank cars need no protective bonding.	Bonding is not required where vehicles are unloaded through closed bottom or top connections. To protect against stray currents, tank car facilities where flammable/combustible liquids are unloaded through open domes shall be protected by permanent bonding.	NFPA 30 Ref. #1 30-36	Yes & No
		When unloading tank cars through closed connections, no protective measures are required.	NFPA 77 Ref. #2 77-39	Yes
		Both rails of railway tracks where unloading takes place should be bonded permanently to each other and to the earthed pipeline.	British Standards Institute Ref. #5 Sec. 9.4.1	No
2.6	Portable metal drums and cans being filed from other containers while both ret on conductive foundations need no further bonding as long as the fill nozzle remains in contact at metallic spout.	In filling metal cans/drums, a conductive fill spout, nozzle of fill pipe should be kept in continuous contact with fill opening. Then a bond wire is not required.	NFPA 77 Ref. #2 Article 580	Yes
		Contact is made between filling nozzle and container before filling starts and throughout filling.	Fire Protection Handbook Ref. #3 5-36 to 5-37	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.6	(continued)	During filling/emptying, container & all metallic parts of system should be bonded together and/or earthed.	British Standards Institute Ref. #5 Sect. 11.2.1, 11.3.3	No
		Placing nozzle of dispensing container in contact with opening of receiving container establishes bond. If this metal-metal contact cannot be maintained, a bond wire should be used between containers.	National Safety Council Ref. #7 5	Yes
		Use bonding wire only if contact is not made or maintained with spout and nozzle.	Handbook of Industrial Loss Prevention Ref. #9 30-7	Yes
2.7	Bonding or grounding of automobiles while being filled at gas station is unnecessary.	To ensure that the vehicle is grounded, rest nozzle firmly on filler pipe.	Swiss Chemical Industry Ref. #9 7	Yes & No: suggests that sparking is there but standard applies to situation for liquid that are much more severe.
	Bonding between tank trucks and underground gas station tanks is unnecessary, provided that hose remains in metallic contact with tank fill pipe or is connected tightly.	No external bond wire or bond wire integral with hose is needed for unloading of flammable liquids into underground tanks.	NFPA 77 Ref. #2 77-35	Yes
		When a delivery is made from a road tanker to a storage tank (for example, at a petroleum filling station) the continuity of the hose coupling between the vehicle & tank is adequate provided it is monitored.	British Standards Institute Ref. #5 Sect. 9.3.2	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.8	Protection against ESD is achieved for filling marine craft if fueling nozzle is kept in metallic contact with fuel tank fill pipe.	Pipelines on wharves shall be adequately bonded & grounded if Class I or Class II liquids are handled.	NFPA 30 Ref. #1 30-37	No
2.9	Regarding aircraft fueling:			
	(a) Bond fuel hose nozzle to plane by means of short bond wire and clip.	In over-the-wing delivery, connect fuel nozzle to metal part of aircraft, and connect aircraft to fuel tank near fill opening using a short bond wire and clip.	NFPA 77 Ref. #2 77-36	Yes
		There should be a direct bond between the aircraft fueling orifice and the metallic end of the fueling hose. In overwing fueling, bond hose nozzle to aircraft by a separate cable.	British Standards Institute Ref. #5 Sec. 15.3.6	Yes
	(b) If small planes are fueled by gas-station-type hose (up to 25 gal/min), bonding is not necessary.	No information.		
	(c) Some laws require plane, fueler & hydrant vehicle to be interconnected by bond wires to low resistance ground (less than 10,000 ohms).	Some regulations require that the aircraft and fueling system be connected by wires to ground.	NFPA 77 Ref. #2 77-36	Yes
		Additional earthing is sometimes provided by means of a bonding cable between the aircraft and an earthing point in the concrete. Connection should be direct from the aircraft to the earthing rod and independent of the fueling vehicle.	British Standards Institute Ref. #5 Sec. 15.3.3	Yes and No
	(d) No bonding required when fueling aircraft through a tight metal-to-metal connection.	With underwing delivery, fueling is through a closed system. Bond connection not required due to inherent metal-to-metal contact.	NFPA 77 Ref. #2 77-36	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.9	(continued)	With underwing fueling, necessary bonding is achieved by the metal-to-metal contact between the hose coupling and the aircraft fueling adapter.	British Standards Institute Ref. #5 Sect. 15.3.6	Yes
2.10	Regarding ship/barge loading:			
	(a) Limit velocity of incoming liquid to 1 m/s until inlet opening is submerged from 0.3 to 2 meters.	For liquids with conductivity 50 pS/m, the flow velocity in pipe entering the tank should not exceed 1 m/s until inlet had been covered.	British Standards Institute Ref #5 Sect. 13.3.4	Yes
		Linear velocity of the liquid in the pipe entering the tank should be kept low until pipe outlet is well submerged.	NFPA 77 Ref. #2 77-39	Yes
	(b) Use inert gas blanketing or conductive additives as an alternative.	An antistatic additive may be used to raise the conductivity of a liquid. Certain sizes of tankers carrying crude oil or other liquids with similar fire hazard must be provided with an inert gas system as required by regulation.	British Standards Institute Ref. #5 Sect. 13.3.5	Yes
	(c) No bonding required because hull of ship is in contact with water and is inherently grounded.	Hull of vessel is inherently grounded by virtue of its contact with the water.	NFPA 77 Ref. #2 77-39	Yes
		Ships of metal construction are inherently earthed because they float in water. All metal fittings, pipework and associated equipment should be earthed to the ship.	British Standards Institute Ref. #5 Sect. 13.2.1	Yes
2.11	Regarding metal storage tanks:			
	(a) Static-generating and static-dissipating qualities of liquid determine possibility of sparking.	Relaxation time depends on the resistivity of the liquid. Provides list of protective measures which depend upon characteristics of liquid being handled.	NFPA 77 Ref. #2 77-28 to 77-31	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.11	(continued)	Discusses static electricity producing characteristics of hydrocarbons.	Fire Protection Handbook Ref. #3 5-36	Yes
	(b) Avoid splash filling; outlet of fill pipe should discharge near bottom with minimum agitation.	Overshot splash filling should be prohibited. Inlet fill pipe should discharged near the bottom and should reduce turbulence to a minimum.	NFPA 77 Ref. #2 77-30	Yes
		Splash filling into a tank where a flammable atmosphere may exist should be avoided. Use bottom entry of a fill pipe reaching to bottom of tank, inlet should be designed to minimize turbulence.	British Standards Institute Ref. #5 Sect. 3.3	Yes
		Filling pipes should be at or near bottom to reduce static & turbulence; direct liquid horizontally; no splash filling.	Handbook of Industrial Loss Prevention Ref. #9 30-7	Yes
	(c) Limit velocity of incoming liquid to 1 m/s until outlet is submerged.	Linear velocity of liquid in the pipe entering the tank should be kept low until inlet is well submerged.	NFPA 77 Ref. #2 77-30	Yes
		For liquids with conductivity 50 pS/m, flow velocity in pipe entering tank should not exceed 1 m/s until inlet has been covered. For storage tanks of road/rail tank size, flow velocity should be calculated according to Section 7.3.3.	British Standards Institute Ref. #5 Sect. 3.3.4	Yes
	(d) In the case of a floating-tank, follow above precautions until roof becomes buoyant; no precautions necessary after this due to absence of flammable vapor space.	When flammable liquids are dumped into a floating roof tank, protective measures are applicable until roof becomes buoyant.	NFPA 77 Ref. #2 77-31	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.11	(continued)	When a liquid with conductivity 50 pS/m is dumped into a metal tank with a floating roof, precautions are applicable until roof is buoyant.	British Standards Institute Ref. #5 Sect. 3.7 & 3.8	Yes
	(e) In the case of switch loading, follow above precautions or ventilate tank to safe vapor concentration before filling.	If tank contains flammable vapor-air mixture from previous use, ventilate tank to 50% or less of the lower flammable limit before dumping in new liquid.	NFPA 77 Ref. #2 77-31	Yes
	(f) Some types of nonconducting floating-roof tank covers have isolated metallic clips which require bonding.	Particular care is needed in systems incorporating metals and high resistivity nonconductors.	British Standards Institute Ref. #4 Sect. 11.3.5	Yes
		Charge accumulated on tanks made of high-resistivity materials presents a hazard for insulated metal components.	British Standards Institute Ref. #5 Sect. 4.1	Yes
2.12	Regarding air-blown agitators:			
	(a) Cause prolific ESD.	Mixing together of liquids gives rise to static electricity ignition risks. Follow usual precautions for liquid handling operations. (See Section 3.)	British Standards Institute Ref. #5 Sect. 10.1, 10.4	Yes
	(b) Protect agitator vessel by inert-gas blanketing or by continuous treating system.	Static is generated when liquids move in contact with other materials. Occurs in operations such as mixing, pouring, dumping, filtering and agitating.	NFPA 77 Ref. #2 77-25	Yes
		General discussion of charging of agitator vessels as well as sampling techniques.	Swiss Chemical Industry Ref. #8 6	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.12	(continued)	Surface charges can be made harmless by partially or wholly inerting the vapor space, or by increasing vapor concentration to above upper flammable limit.	NFPA 77 Ref. #2 77-30	Yes
	(c)Centrifuges generate substantial ES charge; protect by inerting or over-riching vapor space.	Bond together containers and filling lines when using mixers/churns.	NFPA 77 Ref. #2 77-40	
		Vapor space in blending vessel can be inerted if antistatic additives are not used.	British Standards Institute Ref. #5 Sect. 10.4.6	Yes
		High charges generated when separating via centrifuge; also due to high velocity of rotating parts. Calls for inerting grounding of metal parts.	Swiss Chemical Industry Ref. #8 7-8	Yes
2.13	Regarding blending tanks & mixers:			
	(a) In-tank jet mixing an high velocity propeller mixing stir up settled water and generate ES charge.	Jet/propeller mixing in tanks may generate charges. Avoid agitating layer of water at bottom of tank. Direct stream so as not to break surface.	NFPA 77 Ref. #2 77-40	Yes
		Keep mechanical agitation to a minimum (air, steam, gas, jet nozzles) because of the charge produced on the mist above the liquid.	British Standards Institute Ref. #4 Sect. 9.3.2.3	Yes
		Jet mixing is not hazardous provided jet does not break liquid surface & that liquid & metal equipment are earthed.	British Standards Institute Ref. #5 Sect. 10.5	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.13 (continued)	(b) Floating-roof tanks are desirable for blending, of if necessary, use gas blanketing.	Inert gas blanketing may be used where flammable mixtures exist above liquid surface. Floating roof tanks are desirable because they eliminate vapor space.	NFPA 77 Ref. #2 77-40	Yes
		Vapor space in blending vessel can be inerted if antistatic additives are not used.	British Standards Institute Ref. #5 Sect. 10.4.6	Yes
2.14	Coating of paint, plastic, or aluminum oxide on inside of cargo or storage tank does not present ES hazard.	Probability of sparking depends on coating thickness. Very thin layers such as paint films & epoxy coatings are unlikely to present a hazard.	British Standards Institute Ref. #4 Sect. 11.2.4	Yes
		Internal coatings such as paint with a thickness less than 2 mm are unlikely to create hazards provided usual liquid handling precautions are followed.	British Standards Institute Ref. #5 Sect. 17	Yes
2.15	Regarding sampling, gauging, level detecting devices:			
	(a) Use natural fiber ropes, not synthetic ropes.	A tape or cord may be made of metal if it is connected to a properly earthed tank or may be made of a natural fiber. A synthetic polymer cord or dip stick is not acceptable.	British Standards Institute Ref. #5 Sect. 6.2	Yes
	(b) Wait 30 minutes after filling large storage or ships' tanks before hand gauging or sampling.	Gauging or sampling through roof opening should be avoided for an interval of time after filling is completed.	NFPA 77 Ref. #2 77-31	
		If tank contains liquid with water phase, wait 30 minutes. If no water phase is present, wait 10 minutes.	British Standards Institute Ref. #5 Sect. 6.3	Yes & No

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.15 (continued)	(c) In tank trucks, rail cards, or smaller volume vessels, wait 1 minute or more before gauging or sampling.	Waiting period of 1 minute for tank trucks and portable containers.	NFPA 77 Ref. #2 77-35	Yes
		If tank contains liquid with water phase, wait 30 minutes. If no water phase is present, wait 10 minutes.	British Standards Institute Ref. #5 Sect. 6.3	Yes & No
	(d) Completely nonconductive hand gauging or sampling devices require no waiting period for charge relaxation.	Gauging/sampling should not be carried out while any charge generating operation is going on unless the liquid conductivity is greater than 50 pS/m.	British Standards Institute Ref. #5 Sect. 6.3	No
	(e) Bond floats of automatic gauging devices to vessel shell through leading tapes and/or guide wires.	All metallic parts of gauging/sampling equipment should be connected to the tank.	British Standards Institute Ref. #5 Sect. 6.2.1	Yes
	(f) Fires caused by static electricity during LP gas sampling rarely occur; fires are confined to open sample containers.	LP gases are normally handled in closed systems where there is no release to the atmosphere. However, flammable concentrations can occur outside the system.	British Standards Institute Ref. #4 Sect. 12	Yes
	(g) Open metal graduates used for sampling must be bonded to fill pipe.	All metallic parts of sampling equipment should be connected to tank.	British Standards Institute Ref. #5 Sect. 6.2.1	Yes
	(h) If graduate is nonconducting, or if a closed-container sampling procedure is used bonding or grounding is not useful.	Sampling equipment made from natural materials should be earthed. Sampling containers from high resistivity materials are acceptable but each case should be assessed by an expert.	British Standards Institute Ref. #5 Sect. 6.2.2, 6.3.3	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.15	(continued)	Use devices that permit sampling on the closed vessel. If not possible, use sampling devices made of nonconductive devices just before they are introduced.	Swiss Chemical Industry Ref. #8 6	Not addressed.
	(i) Alarms or detectors used in the presence of flammable vapor-air mixtures should be made of nonconductive material or be properly bonded.	No information.		
2.16	Regarding abrasive blasting: (a) Sparks have been observed jumping from unbonded rubber hose to grounded objects during grit blasting. (b) Special hoses with built-in metallic shielding to prevent sparking are available from vendors. (c) Within stream pattern, no flammable concentration is likely to exist because of sweeping action of air stream.	No information.		
2.17	Regarding purging and cleaning of tanks and vessels:			
	(a) Steam jets generate prolific charge on nozzle and insulated objects on which the stream impinges.	Wet steam escaping into the atmosphere can generate static electricity. Surfaces on which steam condenses may accumulate static unless properly bonded.	NFPA 77 Ref. #2 77-41, 77-59	Yes
		Compressed air or steam containing particles of condensed water vapor often manifests strong electrification when escaping.	Fire Protection Handbook Ref. #3 5-37	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.17	(continued)	Charge may be left on equipment (pipes or nozzles) with which the gas makes contact. charge is shared with any object on which the gas impinges. May induce a potential on any insulated conductor in its vicinity.	British Standards Institute Ref. #4 Sect. 12	Yes
		Most tank cleaning techniques can give rise to ES charge. Becomes hazardous if charge is retained on insulated conductors in the presence of a flammable vapor-air mixture.	British Standards Institute Ref. #5 Sect. 14.1	Yes
		High velocity steam may generate considerable static in passing through the feed pipe.	National Safety Council Ref. #7 5	Yes
	(b) All conductive insulated objects subject to impingement or condensation, including discharging pipe, should be bonded to tank or equipment, or be grounded.	Bond or ground conductive items contacted by particle-containing gas to discharge pipe. Make sure resistance is less than 10 ohms.	NFPA 77 Ref. #2 77-41, 77-59	Yes
		Bond together and earth all metallic equipment in the system and also any metallic parts on which the gas may impinge. Avoid the use of nonconductors in vicinity of gas streams.	British Standards Institute Ref. #4 Sect. 12	Yes
		Bond & earth all metallic components in the system so resistance is less than 10 ohms. Assess effects of high resistivity materials. Check flammable atmosphere in tank space.	British Standards Institute Ref. #5 Sect. 14.2 & 14.3	Yes & No
		Bond steam hose nozzle & steam lines to vessel, even if using conductive hose. Check for insulated objects present in tank.	National Safety Council Ref. #7 5	

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.17 (continued)	Regarding the use of CO_2 in tanks & vessels:			
	(a) Jet of CO_2 generates static due to CO_2 snow.	Liquid carbon dioxide discharged under high pressure & converted to "snow" causes static accumulation on discharge device & receiving container.	NFPA 77 Ref. #2 77-41	Yes
		Release of liquid carbon dioxide results in a highly charged mixture of gas and "snow".	British Standards Institute Ref. #4 Sect. 12	Yes
		Charge separation occurs at orifice and equal & opposite charges are produced on the orifice & Particulate gas stream. Any unearthed object in the vicinity can acquire a charge from the cloud.	British Standards Institute Ref. #5 Sect. 23.1	Yes
	(b) Putting CO_2 in vessel in form of dry ice and allowing to vaporize is acceptable.	Whatever substance is used for inerting, it is advisable to introduce it slowly through a large orifice to avoid raising spray in vessel.	British Standards Institute Ref. #5 Sect. 23.5.3	Yes
	(c) CO_2 extinguishers should not be used for inerting.	Potentials up to 12 kV have been measured on the nozzle and on an impinged insulated metal object. Presents hazard if CO_2 is used for inerting & precautions are not taken.	British Standards Institute Ref. #4 Sect. 12	Yes & No
		Inerting of vessels containing flammable gas mixtures should be done only with gases that do not condense to a liquid or solid phase when released at high pressure unless it is known that a hazardous potential will not be developed.	British Standards Institute Ref. #5 Sect. 23.4 & 23.5	Yes & No

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.17	(continued)	Do not inert with CO_2 gas or liquid because it forms highly charged dry ice crystals.	Swiss Chemical Industry Ref. #8 6	Yes
2.18	Regarding belts:			
	(a) If pulley is made from conductive material, charge will be dissipated through shaft & bearing.	Metal pulleys will pick up charge from belt and transfer it through shaft and bearing to earth. Use bonding as a precaution where wear and tear on bearings is high.	NFPA 77 Ref. #2 77-53 to 77-54	Yes
		Mere contact with a metal roller leaves charge on the surface of rolling material; rapidly dissipates provided that machinery is properly earthed.	British Standards Institute Ref. #5 Sect. 26.1	Yes
	(b) Use belt made of conductive material or apply conductive dressing.	Static generation can be prevented by making the belt conductive by applying special dressing.	NFPA 77 Ref #2 77-50	Yes
		Conductive belting shall be used in locations where static is a hazard.	Army Safety Manual Ref. #6 7-1	Yes
		The best method to prevent excessive accumulation of static is to use conductive rubber belting. Also can coat belts with a conductive belt dressing.	National Safety Council Ref. #7 5	Yes
		Use belts, pulleys of conductive material.	Swiss Chemical Industry Ref. #8 13	Yes
		Flat belts and V-belts must be conductive. If in doubt, always check.	Swiss Chemical Industry Ref. #8 14	Yes & No

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.18 (continued)	(c) Avoid use of flat belts in hazardous areas; V-belts are acceptable.	Rubber/leather flat belts running at moderate or high speeds can produce sparks several inches long. V-belts are not as susceptible to hazardous static generation as flat belts.	NFPA 77 Ref. #2 77-50, 77-52	Yes & No
2.19	Regarding filters and relaxation chambers:			
	(a) A liquid of low conductivity will accumulate static charge when pumped through a pipe; charge will dissipate when a voltage builds up.	When electrical resistivity exceeds 10^{15} ohm-cm or is less than 10^{10} ohm-cm, net static generation or accumulation is negligible.	NFPA 77 Ref. #2 77-26 to 77-27	Yes & No
		As liquid leaves conducting pipe, it is no longer subject to charge separation process & charge relaxes back to wall of pipe. Also discusses insulated piping.	British Standards Institute Ref. #4 Sect. 9.1.1	Yes
		Extent to which charge is retained depends upon resistivity of pipe material & conductivity of liquid. Discusses high resistivity pipeline & buried pipeline in detail.	British Standards Institute Ref. #5 Sect. 19.1, 19.3, 19.4, 19.5	Not addressed
		Completely fill pipe to exclude possibility of explosive mixture formation in pipe.	Swiss Chemical Industry Ref. #8 3	Not addressed
	(b) Presence of a filter can produce 10-200 times more charge in a system; no danger as long as liquid is kept in closed system.	Recent tests indicate that some filters are able to generate charges 10-200 times higher than that seen in a system without a filter.	NFPA 77 Ref. #2 77-25	Yes

COMPARISON OF RP 2003
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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.19	(continued)	Coarse filters present no static problems. Fine particle filters are prolific static electricity generators. Cannot predict charge generation created by a filter.	British Standards Institute Ref. #4 Sect. 9.1.3	Yes
		Charge densities are up to several orders of magnitude greater than those encountered in pipelines without filters.	British Standards Institute Ref. #5 Sect. 16.1	Yes
	(c) At least 30 sec of relaxation time between filter & discharge point is necessary.	For liquids with conductivities ≥ 2 pS/m, residence time should be 30 sec. Below 2 pS/m, use 100 seconds.	British Standards Institute Ref. #5 Sect. 16.3	No
		Consult specialist when filters are used.	Swiss Chemical Industry Ref. #8 3	No
	(d) Relaxation time provided by sufficient piping volume.	Charge generated in filter can be dissipated by including a metal relaxation chamber in pipeline. In some cases, pipeline itself is long enough.	British Standards Institute Ref. #5 Sect. 16.3	Yes
	(e) Ignore relaxation criteria for liquids with conductivities ≥ 50 pS/m	For liquids with conductivities above 2 pS/m, relaxation time should be 30 seconds.	British Standards Institute Ref. #5 Sect. 16.3	No
2.20.1	Buried plastic tanks do not present an electrostatic discharge problem.	Possibility of incendive discharge from surface of buried high resistivity tank cannot be dismissed. Tanks should be individually designed. Only conductive non-metallic tanks present no additional hazards.	British Standards Institute Ref. #5 Sect. 5.1, 5.2, 5.3	No

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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.20.2	Test sample of aboveground GRP tank showed conductivity 100 times as great as a typical liquid product being handled.	No information.		
	In tests where fuel was dumped into an aboveground insulated plastic tank, metallic fittings showed accumulated potentials of up to 11 kV.	No information.		
	Bond together & ground all external metallic objects contacting outside of aboveground plastic tank.	Discusses induction charging & charge sharing in relation to unearthed metal equipment & unearthed personnel in vicinity of charged high resistivity items.	British Standards Institute Ref. #4 Sect. 11.2.6, 11.3.5	Yes
2.20.3	Bond only the metal parts on a plastic container to fill pipe.	Discusses high resistivity nonconducting materials in detail. No general resistance value to earth can be suggested. Safety measures should be developed on an individual basis.	British Standards Institute Ref. #4 Sect. 11.3.5, 14.3.3, 14.3.5	No
		Discusses containers made from high resistivity materials in detail. Depends on where container is being used.	British Standards Institute Ref. #5 Sect. 12.1 - 12.5	Not addressed
		Containers made of nonconducting material do not need to be specially bonded or grounded.	Handbook of Industrial Loss Prevention Ref. #9 30-7	No
2.20.4	Avoid sheet plastic for lining drums; lab tests show incendiary sparks.	Sheeting made from high resistivity materials can become charged by various processes, causing a possible ignition hazard. Discusses use of sheeting in different zones.	British Standards Institute Ref. #5 Sect. 25	Yes

COMPARISON OF RP 2003
WITH OTHER STANDARDS

RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.20.4	(continued)	Discusses metal containers with outer non-metallic coatings/jackets in relaxation to ESD hazards.	British Standards Institute Ref. #5 Sect. 18	Yes
2.20.5	Static ignition of petroleum vapors by wearing apparel constitutes low hazard. Not necessary to ground personnel or provide antistatic clothing.	Locations where flammable liquids & gases are handled should be studied carefully to determine effect of personnel charging. Establish individual guidelines.	NFPA 77 Ref. #2 77-12 to 77-13	No
		If personnel are sufficiently insulated from earth, sparks can arise that can ignite flammable mixtures or cause electric shocks. Discusses nature of sparks from bond/clothing & safety precautions.	British Standards Institute Ref. #4 Sect. 13	No
		Earth personnel in contact with flammable vapor with MIE up to 100 mJ. Antistatic clothing not required in presence of vapor-air mixture with MIE greater than 0.2 mJ.	British Standards Institute Ref #5 Sect. 29.3, 30	No
		Many flammable liquids & air mixtures can be ignited by static discharge from a person. Recommend use of conductive floors & shoes.	Army Safety Manual Ref. #6 7-2	No
		Personnel receiving shocks can cause accidents. Body can accumulate high levels of static charge in low humidity conditions, causing a hazard. Recommend natural fabrics & grounding via shoes.	National Safety Council Ref. #7 1, 3-4	No

COMPARISON OF RP 2003
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RP 2003 SECTION	WHAT RP 2003 SAYS	WHAT OTHER STANDARDS SAY	STANDARD REF	IS RP 2003 RECOMMEN-DATION SUPPORTED
2.20.5	(continued)	Ground personnel; install conductive floor coverings.	Swiss Chemical Industry Ref. #8 21	No

APPENDIX C

ELECTROSTATIC HAZARDS LITERATURE SOURCES

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APPENDIX D

MONOGRAPH

AMERICAN PETROLEUM INSTITUTE
STATIC ELECTRICITY RESEARCH PROJECT

MONOGRAPH

ELECTROSTATICS IN THE PETROCHEMICAL INDUSTRY

Laurence G. Britton

This monograph is based on the assumption that the API will sooner or later extend its recommendations to all flammable liquids handled in the Petrochemical Industry. The existing API RP2003 was developed for the safe handling of petroleum distillates such as naphtha, gasoline and other fuels. The industry is increasingly involved in the handling of additives (alcohols, ethers), solvents and processed products. These products can be quite unlike simple hydrocarbons in their ranges of flammability, ignition energy, and conductivity. In many cases the use of antistatic additives is not an option owing to product contamination (although in the case of solvents there is frequently the option of blending a non-conductive solvent with a compatible conductive solvent to create a mix that does not accumulate static). Quality control and other forces are increasing the use of microfilters, often in conjunction with plastic components and plastic linings; as a result simple "relaxation" considerations are no longer sufficient in all cases to determine the conditions for static accumulation. European practice has introduced the general requirements for personnel grounding, and much work has been done in the area of plastic hazards. Words such as "brush discharge", and "propagating brush discharge" are in common use but are not found in API RP2003.

In some parts of this monograph it has been necessary to refer to terms such as "inertion", "flammable limits" and "minimum ignition energies". Also, the usual definition of "flammable liquid" needs to be made more workable. The first few pages are therefore devoted to these considerations. Appendices are provided giving extensive listings of liquid conductivities, ignition energies and other properties, derivations and discussions of subjects summarized in the text, plus a cross-referenced literature survey. While the presentation attempts to be general in its considerations for liquid handling, a principal focus is upon the present text of RP 2003.

Highlights:

- *While Figure 1 in API RP2003 is a good approximation for fuels such as paraffinic mixtures with regular ASTM distillation curves it is erroneous for many single component hydrocarbons and other flammables. A better illustration is recommended for these cases and Figure 1 should be accompanied by a use limitation statement including a caveat about mist and foam ignition. The ignition energy of mist below about 30 micron diameter converges to that of a vapor. Very fine mist can be produced during splash filling and as foam breaks up.*

- *It should be noted that exponential relaxation (above about 2 pS/m) is not governed solely by "rest conductivity" as measured in the laboratory. The effective conductivity in the field is significantly reduced by reduction in temperature (for example from about 100 pS/m at 25 C to about 30 pS/m at -10 C). Further, highly charged liquid may display a relaxation time that is up to one order of magnitude greater than predicted (this effect is usually unimportant unless a microfilter or other source of high charging is present). To address the temperature problem, either the nominal "static accumulation" conductivity might be raised to 150 pS/m, or a temperature correction can be made, or the conductivity measured at the temperature of interest.*

- *The velocity-diameter limit developed experimentally for tank truck filling only holds for smooth-bore pipes and hoses during overhead filling via a dip pipe. Products between 0.36 and 0.50 m^2/s are suggested in the literature, while higher values may be used for compartment lengths greater than 2 m. For bottom connection filling (which can be more hazardous and not less hazardous as stated in RP2003) the product should not exceed 0.36 m^2/s and the inlet should be fitted with a deflector to prevent jetting. Composite hoses containing an internal grounding spiral should be avoided when loading non-conductive flammables because of the excessive static generation apparently caused by the spiral, especially in hoses of small diameter. To allow for the limited test conditions under which the API velocity-diameter limit was developed (uniform charge distribution, no free water etc.), and some fires which have occurred at low product values, it should be stressed that a lower v•d product is desirable particularly for bad actors like toluene. An important point to make is that for equal values of v•d product, the maximum safe filling rate is proportional to filling pipe diameter. Where there is a choice, larger diameter pipes are intrinsically safer. This is additionally important for rough bore (spiral wound etc) hoses where for smaller diameters the blockage ratio and charging should be greater. Rubber boots on the end of dip pipes should be conductive.*

- *A potential problem with wound composite hoses is that the inner spiral is often not attached to the end connectors and in some cases the gap is an effective spark source during draining of non-conductive liquid from the hose. To avoid this hazard, a semiconductive liner may be used. Alternatively, the hose can be designed to provide bonding via the inner spiral. To show that the inner spiral is bonded, one design uses an isolated outer spiral and other designs (such as an outer spiral bonded to a single, grounded end connector to avoid complete isolation) might be specified.*

- *Section 2.4.2 in API 2003 states that non-conductive hose can be used provided the end connector is bonded. Use of non-conductive hose for non-conductive flammables is hazardous since discharges may occur on the surface. At high levels of charging, such as downstream of a filter, powerful propagating brush discharges may occur. The meaning of the statement made that "continuity is not required in bottom or top loading through tight connections" is unclear.*

- *Hoses (and pipe) containing a continuous non-conductive liner may undergo pinhole puncture by small propagating brush discharges when charged non-conducting liquid accumulates surface charge on the liner. This is most likely to occur downstream of filters. The problem has occurred in steel flexible hose with extruded thermoplastic liner, where repeated puncture at a point caused leakage. With composite hose containing a coated spiral any pinholes will go to this spiral rather than through the carcass, so since leaks should not be caused the phenomenon probably has not been noticed. It is unknown whether there is an ignition hazard due to these discharges, which would require them to occur after a flammable gas mixture has formed, such as at the end of filling. This type of discharge can be avoided using a semiconductive liner (metal or carbon filled polyolefin) or any type of hose with internal bare metal surfaces such as an uncoated inner spiral.*

- *Figure 7 shows what appears to be a close-coupled filter in drum filling and states that the hose can be non-conducting. Both are extremely dangerous for non-conductive flammables as is well supported by literature and by accident histories.*

- *Purging recommendations should refer to NFPA 69 to generalize the coverage.*

- *The 30 second residence time downstream of a filter is not conservative for liquids of very low conductivity (less than about 2 pS/m) and should be increased to 100 seconds. This is proved theoretically and is verified by published test work. The reason for this need is that filters generate high levels of charge even at low conductivity; even were this not the case the charge density dependence of hyperbolic relaxation makes the time taken to relax to acceptable levels (20 - 30 $\mu C/m^3$) almost independent of the initial charge density above about 100 $\mu C/m^3$. Temperature effects on conductivity should be considered to make 2 pS/m a meaningful demarcation. Note that the NFPA and BS guidelines calling for "3 relaxation times" residence would require 27 seconds for a typical hydrocarbon at 2 pS/m which is close to the "worst case" 30 seconds presently given by API. However, below 2 pS/m the 100 seconds criterion should be applied.*

- *While 50 pS/m is a useful demarcation for static accumulation in grounded equipment, it does not represent the conductivity level above which a liquid is "conductive". This has been drawn at various levels according to the handling operation involved. 10000 pS/m is a conservative "ceiling" level while 1000 pS/m has been established as a "safe" conductivity for almost all operations, including those involving stirred slurries and pipes / hoses lined with high resistivity material. Other levels (for example 200-300 pS/m) have been applied to certain military applications such as warplanes.*

- *Plastic containers and equipment are responsible for many fires and injuries and the present coverage is entirely inadequate. In the case of FRP and other plastic aboveground tanks, splash filling must not be done. There was a recent FRP tank explosion involving splash filling of a conductive liquid; conductive liquids give rise to surface sparks rather than brushes and only a few kV is needed to ignite vapor. It is important to stress that with plastic containers there is no safe liquid conductivity. Sparks from conductive liquids can be produced by splash filling or simply rubbing the outside of the container, which induces very high potentials in the liquid. A charged plastic surface can give rise to incendive brush discharges or may induce hazardous potentials on nearby conductors. Even plastic tubing and small sample bottles have caused fires.*

- *It is untrue that special measures to ground personnel are not necessary; for example, there is some evidence that ungrounded personnel are a direct or indirect cause of hose fires following tanker filling. In the industry in general, ungrounded personnel are a frequent cause of fires when handling flammable liquids and grounding is often recommended in codes. It is true that clothing is not usually a problem unless it is removed causing crackling discharges (brush types). The type of clothing can determine the charge on an ungrounded person, however. Personnel grounding may be achieved using a variety of commercially available devices (conductive/antistatic shoes, foot grounders, bracelets) and commercially available accessories such as conductive paint for floors, and resistance testers to ensure the devices are operating properly.*

- *To avoid stray currents in wharf lines an insulating flange (commercially available) should be installed. Non-conductive hose should not be recommended.*

- *RF stray currents in the vicinity of radar and radio transmitters should be addressed. Shell has published a nomograph allowing ignition hazard field strength thresholds to be found for methane and hydrogen with respect to source frequency and the loop perimeter of any adventitious antenna.*

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INTRODUCTION

This Monograph and Literature Search was written in partial fulfilment of Technical and Cost Proposal No. 8906-004, by C. James Dahn of Safety Consulting Engineers Inc., to the Americal Petroleum Industry Committee on Safety and Fire Protection. Primarily it fulfills Phase I : Tasks I and IV of the Proposal. However, by writing in Monograph format, it was possible to largely address all areas of the Proposal. Safety Consulting Engineers Inc. will separately develop the comparisons of RP 2003 with Literature and Standards, which will be presented in tabular format for summary use.

In view of the limited development time available, it has been written primarily as a resource document rather than a comprehensive text. It has been necessary to omit any discussion of powder handling except where this relates to stirred slurries or powder addition to flammable liquids. The document is written in WORD version 4.0 for the Macintosh, making use of CA-CRICKET GRAPH version 1.3.2 and MACDRAFT version 2.0 software packages.

The first section of this monograph deals with a working definition for "flammable" that can be applied to all cases, irrespective of location or handling temperature. Next, specific handling recommendations are developed based on liquid conductivity and equipment used. In a first appendix, a discussion of the concept of "conductivity" and its practical limitations is made. In a second appendix, an extensive listing of conductivities and other dielectric properties is given. A third appendix lists ignition energies and "most sensitive" compositions for ignition. A fourth appendix lists Limiting Oxygen Concentrations (LOCs). Subsequent appendices discuss charge generation and accumulation processes in liquid handling, and simple mathematical models. Some theoretical aspects of charged non-conductive surfaces are discussed. The conclusions are summarized in the text.

By courtesy of API, extracts of this Monograph were submitted for publication in "Plant/Operations Progress" and the paper is scheduled to appear in the April 1992 issue. A copy of the paper is attached.

FLAMMABILITY

Flammable and Combustible Liquids

The definitions given in NFPA 321 "Basic Classification of Flammable and Combustible Liquids " are:

Flammable Liquid : A liquid having a flash-point below 100 °F (37.8 °C) and having a vapor pressure not exceeding 40 psia (2068.6 mmHg) at 100 °F (37.8 °C). Materials with higher vapor pressures are considered to be flammable gases.

Combustible Liquid : A liquid having a flash-point at or above 100 °F (37.8 °C).

As explained under "Flash-Point" below, it is prudent in general application to consider that a liquid handled at a temperature greater than the "closed cup flash-point minus 10 °F" might form flammable mixtures under certain conditions.

Flash-Point (Lower Flash Point)

The flash-point is the minimum temperature of a liquid at which sufficient vapor is given off to form an ignitible mixture with the air near the surface of the liquid or within the vessel used as determined by appropriate test procedure and apparatus as specified. Further definitions and test methods are given in NFPA 321 "Basic Classification of Flammable and Combustible Liquids".

In this document the closed-cup flash-point will be referred to exclusively. This is because the closed-cup simulates the attainment of vapor-liquid equilibrium as is the ideal case in closed containers. Closed cup flash-points are typically at least 10°F lower than for the open-cup, in which vapor is continually convected away from the surface. If minor components of low flash-point are present in a bulk liquid, these might not show up in an open cup test. However, the concentration of these components might be critical to the formation of a flammable atmosphere in equipment. Even the closed cup might not adequately represent the gas-space conditions in a nearly full, large tank, where minor components or degassing processes might greatly exceed the flammable component concentrations attainable in the small closed cup apparatus. An example would be degassing of dissolved hydrocarbon gases from oils following temperature changes, pressure changes or turbulence, especially in a nearly full tank.

The average pressure at latitude 50 °N and an elevation of 2 km (1.25 miles) is only 11.5 psia (595 mmHg) as opposed to a standard 14.7 psia (760 mmHg) at sea level. As elevation increases, ambient pressure falls and liquids evaporate faster. As a result, a greater fuel fraction is present in the equilibrium vapor and the flash-point falls. A "rule of thumb" for estimating this effect will be given in the 1991 edition of NFPA 325M:

Flash-point at pressure of interest (°F) = {Flash-point at 760 mmHg pressure}

minus {0.05 x (760 - ambient pressure, mmHg)}

By this rule, at high elevations such as Denver and Mexico City (1-2 miles) the effect is small but significant (about 8°F at 1.25 miles). Owing to this effect, compounded by local changes in atmospheric pressure and reproducibility errors in the original flash-point measurement, it is prudent to consider that a liquid handled at up to 10°F less than its listed flash-point might flash under certain conditions.

Working Definition of "Flammable Liquid"

To account for reproducibility and other flash-point errors, plus to allow for special precautions for liquids handled above ambient temperature, the following definition is suggested:

Flammable Liquid : "A liquid handled above its flash-point, or within 10°F of its flash-point, where flash-point is measured by closed cup"

With regard to small ignition energy sources such as static electricity, this definition incorporates a further margin of safety since the ignition energy at the flash-point composition is very high (of the order 1 or 10 Joules). The flash-point is determined using a naked flame. It requires richer compositions, and correspondingly higher liquid temperatures, for the vapor to become susceptible to ignition by most static discharges.

This definition best applies to single component liquids. Where blends are involved and there is less certainty in the flash-point, a larger safety margin might be necessary. Klinkenberg [1, p.22] suggested 15 °C below the flash-point as indicating non-flammability for petroleum distillates. Where significant mist formation is possible, no flash point consideration is valid (see Appendix C). Liquid foams (froths) may also burn below the flash point but the extent of combustion will normally be limited to the volume of disrupted foam which "mists" and evaporates as any flame propagates through or close to it.

Figure 1 : Flash-Points of Liquid Mixtures with Non-Flammable Components

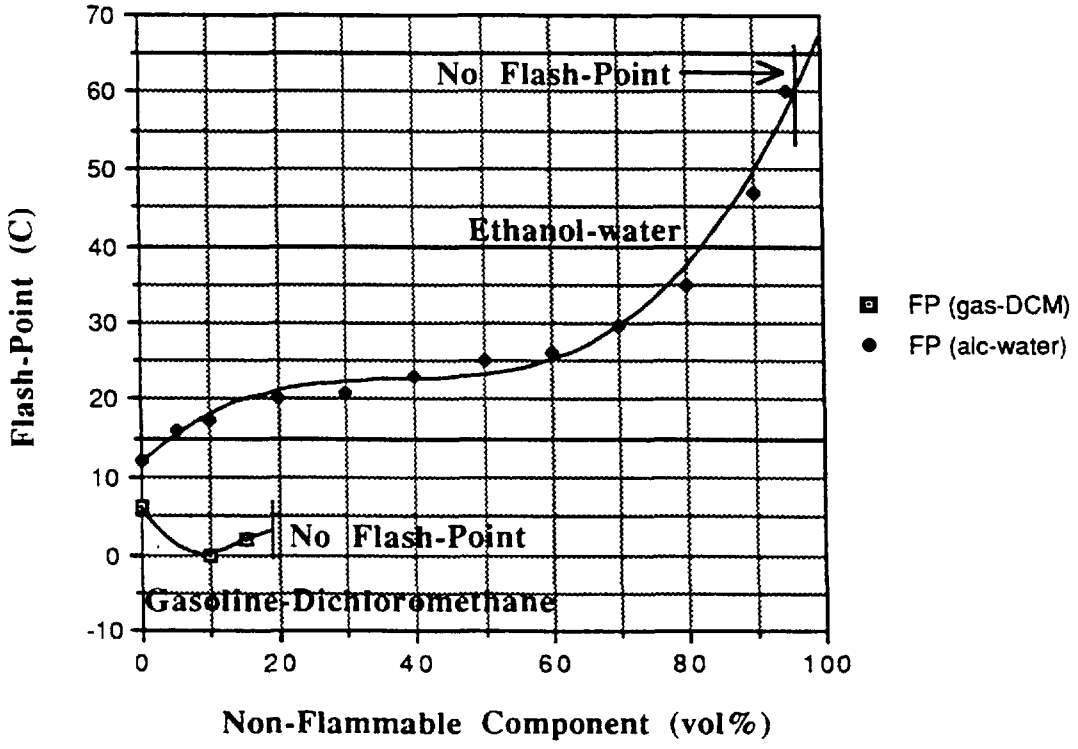


Figure 1 [84] shows two cases first where a higher boiling non-flammable component (water) is added to ethanol and second where a lower boiling non-flammable component

(dichloromethane, DCM) is added to gasoline. In the first case, the flash-point of ethanol is increased with the addition of water (the figure neglects the azeotrope at high ethanol concentration). In the second case, the flash-point of the gasoline (IBP = 115°C) initially decreases as the lower boiling DCM (BP = 40°C) is added, but then begins to increase. Above 20 vol% DCM no flash-point is exhibited. However, with continued evaporation the mixture will become depleted of DCM and become flammable again. Similar effects are found with initially non-flammable mixtures of ethylene oxide and Freon R-12 (dichlorodifluoromethane), where free evaporation of the non-flammable liquid mixture will deplete the lighter non-flammable component and the residual mix can eventually flash. A further point regarding the gasoline-DCM curve is that although mixtures containing more than 20 vol% DCM will not initially flash in the closed cup tester, the vapors are in fact flammable given larger sources of ignition. Thus, in listings such as NFPA 325M and NFPA 49, flammable limits are often cited for liquids having no flash-point. This is a highly confusing state of affairs, but there is great opposition from some quarters for changing the classification of such materials (mostly halogenated hydrocarbons) from non-flammable to flammable. To summarize, initially non-flammable mixtures may become flammable by depletion of more volatile components. This is a case where open cup techniques may be useful. Also, some vapors of high ignition energy and large quenching distance may produce flammable mixtures in air yet have no flash-point. The latter concern is not relevant to most static ignition sources (which are weak) but instead to high energy sources such as flames and welding arcs.

It is necessary to consider OSHA's rule in 1910.106 (a) (18) (b) (iii) which requires that when a combustible liquid (FP > 100 °F) is heated to within 30 °F of its flash-point it shall be handled in accordance with the requirements for the next lower class. For example, Class IIIB liquids (FP > 200 F) must be treated as Class IIIA (140 °F < FP < 200 °F), Class IIIA must be treated as Class II (100 °F < FP < 140 °F) and Class II must be treated as Class IC (that is, a "flammable" liquid by the definition of a flash-point less than 100 °F). From OSHA's perspective, all liquids having a flash-point less than 130 °F should be treated as flammable. As noted in the previous paragraph, 15 °C (~ 30 °F) has been suggested to give a flash-point safety margin for distillate mixtures. Whatever safety margin is used, it is necessary to comply with the OSHA requirements. The 10 °F safety margin (which is considered more realistic for single components) can be used to indicate where special precautions should be taken.

Upper Flammable Limit Temperature (Upper Flash Point)

It can be hazardous to establish non-flammability based on the upper flammable limit (UFL) or the temperature at which this limit is exceeded under equilibrium conditions. This is primarily because flammable volumes may exist locally in a vessel due to non-equilibrium, temperature gradients and air ingress. For water soluble liquids, it is not always appreciated that water addition can render vapor spaces flammable by affecting vapor-liquid equilibrium, a classic case being water-ethanol mixtures (HERC Tech Notes Number 3). Above about 42 °C the equilibrium vapor above 100% ethanol is above its UFL. However, if water is added the vapor space is rendered flammable at much higher temperatures (for instance, at least 60 °C at 80 vol% dilution with water).

Limiting Oxygen Concentration

The limiting oxygen concentration (LOC) is the lowest concentration of oxygen given in volume percent at which a fuel at any concentration can propagate a flame under conditions specified by test. To render an atmosphere inert the oxygen is reduced to some specified fraction of the LOC by adding inert purge gas. The requisite concentration of oxygen depends on the fuel and the required margin of safety. The requirements are given in detail in NFPA 69 (1986 Edition) Chapter 2, and a table of LOCs is given in Appendix C of the Standard. Very few data are available for oxidants other than oxygen.

Safety Margin Appendix A in NFPA 69 requires that where oxygen content in a vessel is continuously monitored the concentration should be maintained at no more than 60% of the LOC. If it is not continuously monitored the maximum should be 40% of the LOC. By Committee action in June 1991, the requisite safety margin was relaxed. In the next edition of NFPA 69 the margin will be 2 vol% below the LOC for continuously monitored oxygen (60% of LOC if the LOC is less than 5%) and 60% of LOC where oxygen is not continuously monitored (40% of LOC if the LOC is less than 5%).

Consider a practical situation in which neither continous nor "spot" tests of oxygen concentration are carried out. In an extreme case, a nitrogen or other purge gas line might be dropped into equipment and left there for an arbitrary time. Neither the flow rate nor flow time has been predetermined using NFPA 69 provisions, or if it has, it is ignored. Gas in the equipment may therefore be well above the LOC and capable of deflagration. This is a particularly hazardous situation since the act of "purging" engenders the idea that the gas has been rendered non-flammable, when in fact it might not have been. While any reduction in oxygen concentration is likely to increase the ignition energy of the vapor mixture, little or no quantitative information is available on the variation of ignition energy above the LOC.

Inerting procedures should be carefully drawn up and followed. For example, the flow rate, flow time, and depth of insertion of a purge gas line to reduce the oxygen concentration to an acceptable level (typically a nominal 5 vol%) can be determined by a series of experiments on a drum or tankcar. Acceptable minimum flow rates and flow times can then be prescribed for identical situations. Such procedures should be subject to scheduled checks using an oxygen analyzer plus maintenance to ensure that the purging equipment is operating properly.

API Vapor Pressure-Flammability Correlation

Figure 2 (adapted from API RP 2003) was compiled for petroleum-based materials and can in form be traced back to Klinkenberg [1, p. 22] who states that it is an approximate correlation for hydrocarbon products having a regular ASTM distillation curve. The original Klinkenberg Figure lines were more divergent than currently shown by API and the two Figures are not equivalent. The two exponential equations shown describe the upper and lower limit lines based on the indicated reference points taken from API RP2003 Figure 1. Figure 2 has obvious uses when mixtures of different hydrocarbons are involved and an assessment of flammability at a prescribed temperature is required from a single vapor pressure measurement. It must be appreciated however that Reid Vapor Pressure is lower than true vapor pressure for multicomponent liquids (average factor 1.09 for gasoline) and can underestimate minor high-volatile component vapor pressures.

The generality of Figure 2 can readily be checked. HERC Data Guides, Kuchta [21] and other sources of vapor pressure can be used to find the vapor pressures of various liquids at 100 °F, while NFPA 325M or HERC Data Guides can be used to find the flammable limits. If the Figure is used for "petroleum products" other than paraffinic fractions the relationship shown is unsafe. Several liquids commonly handled in the Petrochemical Industry were examined:

dioxane (VP ~ 1.54 psi @ 100°F, flash-point = 12°C, upper limit attained @ 57°C)

Figure says liquid will only flash between about -13 and 22 °C. Upper limit is unsafe.

butylene oxide (VP ~ 5.79 psi @ 100°F, flash-point = -15°C, upper limit attained @ 21°C)

Figure says liquid will only flash between about -40 and -8 °C. Upper limit is unsafe.

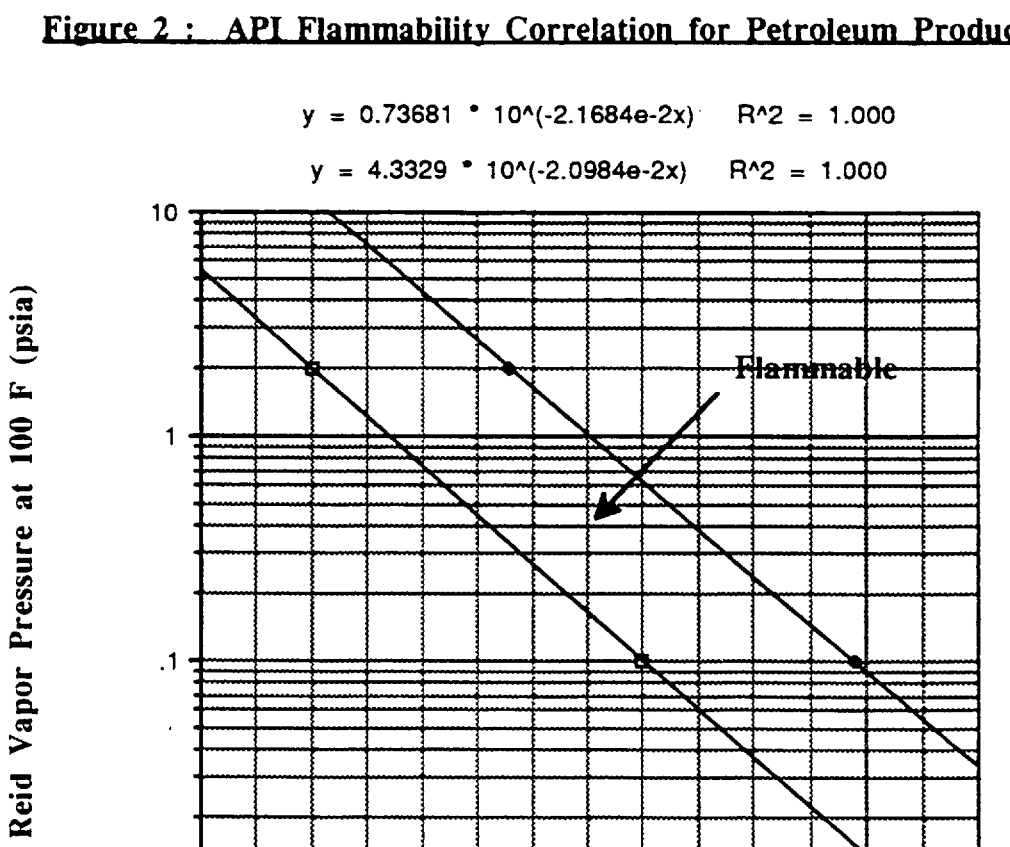
dibutyl ether (VP ~ 0.31 psi @ 100°F, flash-point = 25°C, upper limit attained @ 65°C)

Figure says liquid will only flash between about 17 and 55 °C. Upper limit is unsafe.

Even cyclohexane, a hydrocarbon, is in error at the upper limit. Its VP is about 3.47 psi at 100 °F, and its flash-point and upper limit temperatures are -17 and +15 °C respectively. While it is difficult to interpolate the logarithmic axis of the Figure, it suggests a flammable temperature range from about -30 to +5 °C. Similar errors exist for the hydrocarbon ethyl benzene. The vapor pressure-temperature-flash-point curves given by Kuchta [21] show differences in the behavior of normal paraffins versus other hydrocarbons. Large errors will always occur in upper limit estimates when the liquid has a large flammable range when compared with normal hydrocarbons.

In general, the use of an equilibrium upper temperature limit is not conservative, since this equilibrium takes time to be established and would never be realized in the vicinity of an open manway, for example. Also, as outlined above, the flash-point (approximate equilibrium lower limit temperature) is a meaningless concept when applied to a mist (or foam). In view of possible application errors using API RP 2003 Figure 1, the limitations to its use and cautions about equilibrium attainment should be noted.

Figure 2 : API Flammability Correlation for Petroleum Products



IGNITION SENSITIVITY

Measures of Ignition Sensitivity

Two measures of ignition sensitivity are the lowest minimum ignition energy, and the temperature at which this equilibrium mixture is formed in air. At the flash-point, the mixture is close to the lower flammable limit (LFL) and the ignition energy is very high, of the order Joules (the flash-point tester employs a naked flame). At this limit, static sparks are in general too weak to ignite the mixture. The minimum ignition energy varies with gas composition as a skewed parabola, reaching the lowest minimum ignition energy (LMIE) somewhere in the middle of the flammable range then increasing to several Joules at the upper flammable limit (UFL). Depending on the liquid, the LMIE of the vapor in air can be about 1 mJ or a small fraction of a millijoule.

Figure 3 : Effect of Liquid Temperature on Vapor Concentration and Ignition Energy of Benzene

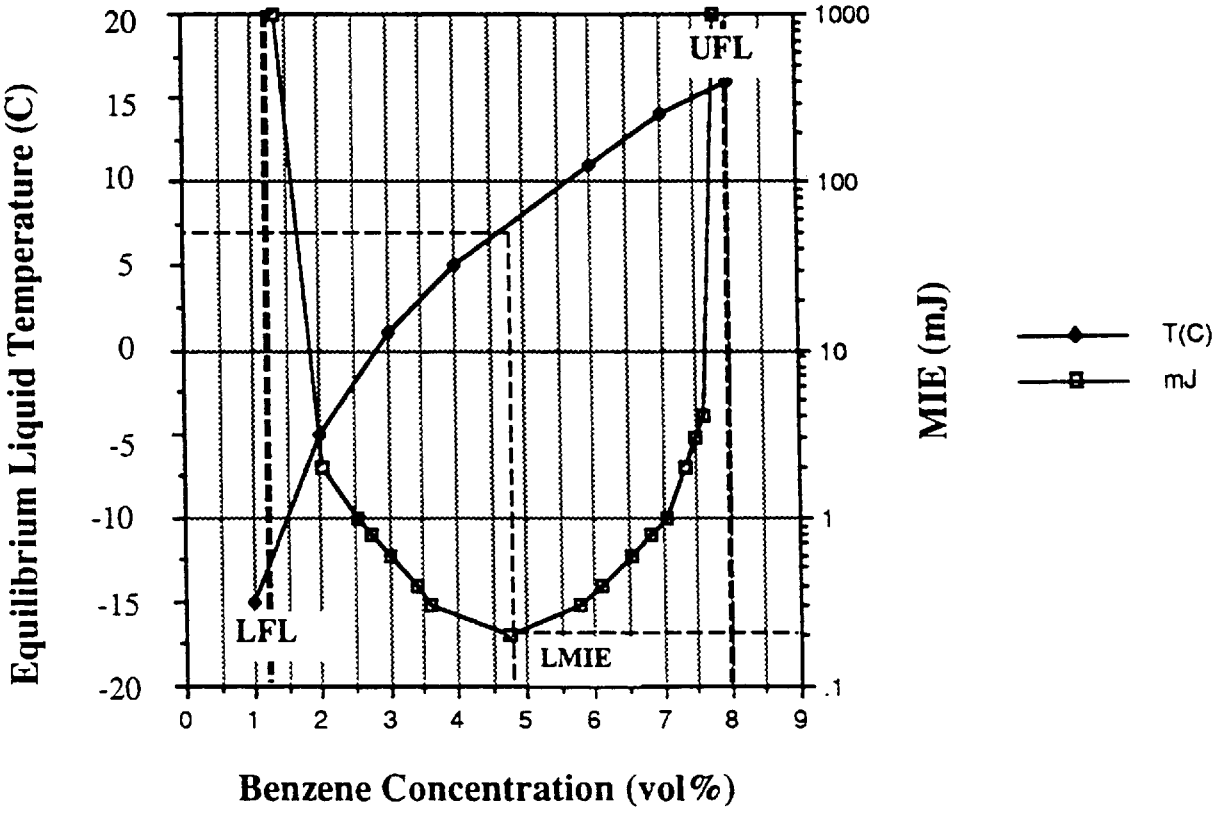


Figure 3 shows how ignition characteristics can be superimposed on a vapor composition curve to show the ignition-sensitive regions, in this case for benzene. Benzene has a flammable range from 1.3 - 8.0 vol%, corresponding to equilibrium temperatures of about -11 and +16 °C. Its stoichiometric mixture (2.72 vol%) is formed at about -1 °C, and its most sensitive composition of 4.7 vol% (corresponding to the LMIE of 0.2 mJ) forms at about +7 °C. As will be shown, brush discharges have effective energies less than 4 mJ, hence brush discharge-sensitive compositions and temperatures can be found from such a graph. While it is true that vapor

equilibrium is slow to be established throughout the vapor space, it is achieved relatively quickly close to the surface and is therefore relevant to surface discharges.

Table 1 shows that the most sensitive (LMIE) composition for many vapors in air occurs roughly half-way between the lower and upper flammable limits. This "rule of thumb" works best with simple hydrocarbons (benzene, heptane) and less well with oxygenated compounds (acetone) or with compounds that have unusually high upper flammability limits (ethylene oxide, carbon disulfide). In many cases the most sensitive composition is 1.5 to 1.75 times the stoichiometric composition (ϕ = fraction of stoichiometric). This composition is formed at an equilibrium temperature significantly above the flash point. Acetone is a poor example, since its most sensitive composition is lean and is formed only about 4 °C above the flash point. However, in other cases the liquid needs to be well above the flash point before the ignition energy nears its minimum value. Thus it can be seen why toluene is so prone to static ignition. Not only is it a non-conductive liquid, but it forms a flammable atmosphere from about 4 - 37 °C and its most sensitive composition is formed at about 26 °C, all well within the range of ambient handling conditions. Benzene is most sensitive at 7 °C, although such a value should be used with caution to allow for non-equilibrium vapor compositions by which the most sensitive mixture can be present at higher temperatures. Xylene isomers should be most sensitive at about 50 °C and the vapors only prone to static ignition at temperatures above the low 30s Celsius.

Table 1. Properties of some Flammable Liquids and their Vapors.

Liquid	LMIE	σ	ε_T	LFL		UFL		(LFL+UFL)/2		True Optimum		
	(mJ)	(pS/m)		(%)	(°C)	(%)	(°C)	(%)	(°C)	(%)	(°C)	(Φ)
acetone	1.15	$5x10^6$	21	2.6	-18	12.8	7	7.7	-4	4.5	-14	0.9
acrylonitrile	0.16	$7x10^5$	38	3	-5	17	28	10	17	9.0	15	1.70
benzene*	0.2	$5x10^{-3}$	2.3	1.4	-12	8.0	16	4.7	7	4.7	7	1.73
carbon disulfide*	0.009	$8x10^{-4}$	2.6	1.0	-30	50	25	25	11	7.8	-16	1.19
cyclohexane*	0.22	2	2.0	1.3	-17	7.8	15	4.6	6	3.8	3	1.67
diethyl ether*	0.19	30	4.6	1.85	-45	36.5	9	19.1	-10	5.1	-28	1.51
ethyl acetate	1.42	$1x10^5$	6.1	2.5	-4	9	19	5.8	8	5.2	8	1.29
ethylene oxide	0.06	$4x10^6$	12.7	3	-18	100	none	52	-5	10.8	-34	1.35
heptane*	0.24	$3x10^{-2}$	2	1.05	-4	6.7	26	3.9	16	3.4	14	1.8
hexane*	0.24	$1x10^{-5}$	1.90	1.2	-22	7.4	5	4.3	-4	3.8	-8	1.7
methyl alcohol	0.14	$1x10^5$	32.6	7.3	12	36	42	21.6	33	14.7	25	1.20
methyl ethyl ketone	0.53	$5x10^6$	18	2	-7	12	22	7	10	5.3	6	1.45
toluene*	0.24	1	2.38	1.27	4	7	37	4.1	26	4.1	26	1.8
xylenes (mixed)	0.2	0.1	2.4	~1.0	~29	~7.0	~62	~4.0	~50	n/a	n/a	n/a

* liquids so marked usually have a rest conductivity below 50 pS/m (non-conductive); this may vary significantly with sample purity and temperature. NOTES:

LMIE	=	Lowest Minimum Ignition Energy (optimum vapor-air mixture)
σ	=	DC rest conductivity of liquid
ε_T	=	Dielectric constant of liquid
LFL	=	Lower Flammability Limit (mol%) of vapor in air; also given is the closed-cup flash point
UFL	=	Upper Flammability Limit of vapor in air; also given is the corresponding liquid temperature
(LFL+UFL)/2	=	First approximation of optimum vapor concentration in air plus corresponding liquid temperature
Φ	=	Fraction of stoichiometric mixture

Conductivity is the reciprocal of resistivity. Conversions: 1 pS/m = $1x10^{-12}$ ohm^{-1} m^{-1} = $1x10^{-14}$ ohm^{-1} cm^{-1}.
Some of the liquids listed have a conductivity exceeding that of pure water ($4.3x10^6$ pS/m). To be "conductive" with respect to static accumulation in grounded equipment, a conductivity of more than 50 pS/m is all that is usually needed.

An important feature of "most sensitive" compositions is that they correspond closely to the mixtures having the fastest burning velocities. Thus, the mixture that is susceptible to ignition by the weakest static ignition source is also that which can give the most violent deflagration. Flammable mixtures are not always uniform in composition.

"Switch-Loading"

Many accidents in the handling of petroleum products have been attributed to switch loading, in which typically a high flash-point liquid such as gas oil or kerosene is loaded into a tanker containing low flash point heels of gasoline or naphtha (etc). Both components can be considered "non-conductive" and miscible. The frequent occurrence of fires during switch loading is attributable only to the existence of a flammable atmosphere in the tank, which would normally be either too rich (gasoline loading) or too lean (gas oil loading) to be ignited by static. This suggests that static accumulation is commonplace and many fires are prevented by the absence of a vapor composition sensitive to small static discharges. The frequent occurrence of toluene tanker fires supports this view, since as discussed above toluene usually creates a vapor space mixture well inside its flammable range, as if switch loading were always taking place.

GENERATION OF STATIC IN PIPES AND HOSES

Streaming Currents in Pipes and Hoses

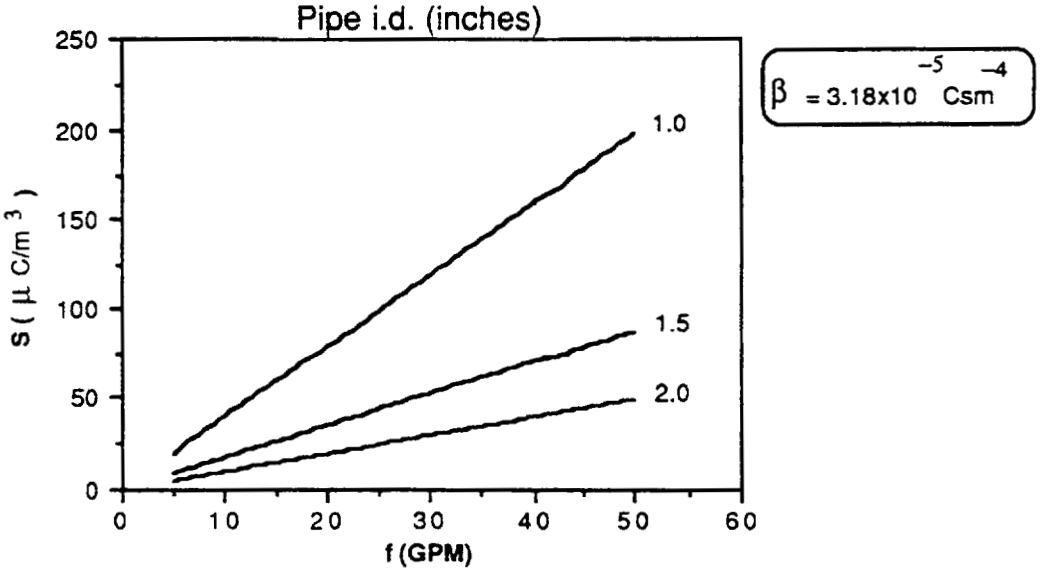
Flowing liquids become charged by a process of preferential ion adsorption at solid interfaces followed by convection of the oppositely charged bulk liquid downstream. Owing to the importance of boundary layer effects, it is both expected and observed that the electrification markedly increases when the flow changes from laminar to turbulent. In the following discussion turbulent flow will be assumed. In pipes and hoses the effluent charge density is found to reach a steady state after a certain length of flow after which the net rate of charge transfer across the wall boundary layer is nil. Theoretical and empirical models (Appendix E) have been developed to predict the charge density convected downstream. Often the effect is described in terms of a "streaming current" (I_S) which can be expressed in Coulombs per second (amperes):

$$I_S = S \cdot A \cdot v \qquad (C.s.^{-1})$$

where	S	=	charge density	$(C.m.^{-3})$
	A	=	pipe cross-sectional area	$(m.^{2})$
	v	=	liquid flow velocity	$(m.s.^{-1})$

Figure 4

Proposed Schon Equation



Appendix E discusses empirical models for estimating the maximum charge density and streaming current in terms of pipe diameter and flow velocity.

Effect of Multiple Phases

The charge density is greatly increased in the presence of a second phase such as solids or non-miscible liquid droplets. In the case of water in oil the charging can increase greatly with little attendant increase of conductivity.

Pro-static Agents

Chemical Hoses

(1) Effect of Non-Conductive Hose

Completely non-conductive hoses such as 100% polypropylene should not be used for transfer of non-conductive liquids. The end connectors are not bonded by the hose and may become spark sources. When charging levels are high (such as downstream of filters) propagating brush discharges can occur causing hose failure and possible fire. The hose surfaces may become charged during handling, for which reason alone they should not be used in flammable atmospheres.

(2) Effect of Non-Conductive Liner

Various types of conductive chemical hoses have non-conductive liners such as polyethylene or Teflon. The liners do not affect the action of the outer metal element (spiral, sheath or steel carcass) in bonding the end-connectors. However, the liners can accumulate charge due to flow of a non-conductive liquid. The charge might be generated in situ by the flow, or deposited from an upstream generator such as a filter. If charging is uniform, it follows that the electric field will be directed radially through the liner and the maximum accumulation will be limited by the dielectric strength of the liner plus any geometric factors introduced by the metal element (such as a spiral).

In 1963 Aeroquip reported [51] failures of fuel hoses consisting of extruded Teflon reinforced with braided stainless steel. The cause of the failures was electrostatic discharges through the liners, appearing as fractures rather than punctures (a network of eroded lines and channels was associated with each pinhole). The discharges did not occur within two inches of the ends of the hoses nor in hoses less than 18 inches long. It is inferred that the pinholes occurred downstream of filters. Time to failure varied from 4 minutes to 2000 hours. The phenomenon was further investigated by the National Bureau of Standards, the Naval Research Laboratory and others [51]. The intention was to set standards for liner conductivity such that charge accumulation leading to pinhole puncture would not occur under the most adverse conditions.

The pattern of failures suggests that the propagating brush discharges responsible for the pinholes do not occur where strong end effects exist but instead require radial field conditions. Thus the pinholes were not observed either in short hoses or near the ends of long hoses, where the adjacent metal connections would introduce an axial field component and (presumably) axial discharges in preferences to discharges through the plastic layer.

The phenomenon was discovered because of leakage from the hoses involved. Whether leakage occurs will depend on the type of hose. For example, a steel flexible hose with braid over an inner plastic liner can puncture and leak because the discharge must penetrate through the entire plastic liner thickness to dissipate to ground. However a composite hose with plastic over a metal inner spiral might puncture to the spiral but not leak, since there are many layers of plastic wrap unpenetrated. Thus, if these discharges are occurring in composite hoses we may not know about it and it is not necessarily a problem anyway.

There is no experimental evidence that non-conductive liners are an ignition hazard, which might be expected in view of the fact that they would normally occur when the line is liquid-full. For ignition, simultaneity of a discharge and a flammable atmosphere in the hose is required. The latter may occur at the end of unloading a liquid such as toluene, where the gas mixture sucked into the hose might well be flammable. During loading, a flammable atmosphere may form in the hose as it drains and air is pulled in from the tank. However, the discharges are caused by liquid flow and are therefore more likely to occur prior to air getting into the hose.

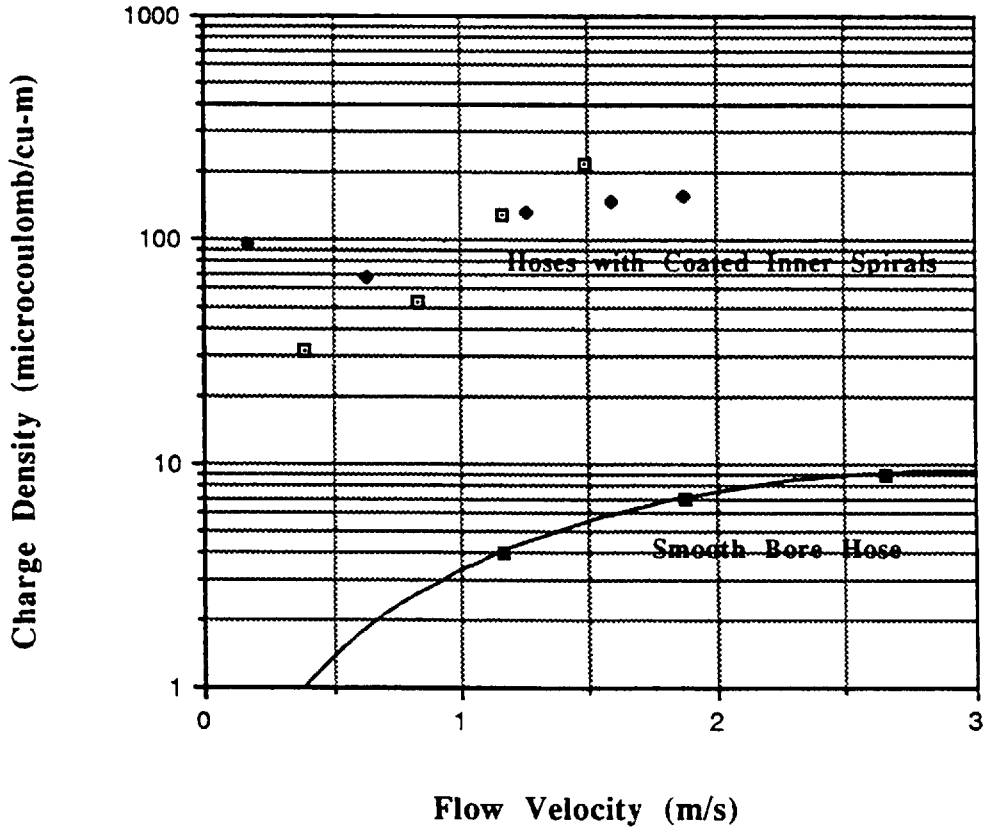
Semiconductive hose liners are available from Peraflex, Willcox and others. Alternatives would be to use a composite hose with no plastic liner on the inner spiral (galvanized or more usually stainless steel spirals might be used) or a convoluted flexible steel hose which has metal sections inside. Any of these should avoid the pinhole puncture problem; the semiconductive liners would conduct the charge away while it is inferred that the steel spiral (or convoluted flexible steel sections) would prevent very high surface charge densities by creating lateral surface fields and by direct conduction of any mobile surface charge layer.

Willcox North America Inc has circulated information ("Incident Data Report No. 7") which blames discharge from a plastic coating on the inner wire of a Compoflex 0951 hose for causing a fire after toluene tanker loading. The available information on this and a similar incident which had occurred immediately previously (same report) does not rule out discharge from ungrounded operators or from decoupled (ungrounded) hoses. Both incidents occurred after disconnection of the hoses and flames exiting the hoses were observed when the hoses were being manually handled. The information does not rule out that a brush discharge might have occurred from the liners as the hoses were handled by their ends, but the spark discharge scenarios probably deserve more attention. One hazard of ungrounded personnel handling an uncoupled hose containing flammable vapor is that the hose can charge as it drains and the ends can spark. Even if the operator is grounded, unless the gloves are antistatic or conductive this event may still occur. Alternatively, charge carried by an ungrounded operator could be the source of a spark.

(3) Effect of Inner Grounding Spiral Roughness

Hoses containing inner spirals may introduce a "roughness factor" which serves to increase turbulence and the effluent charge density may be increased significantly [7]. Figure 5 shows how the charge density of kerosene was increased in 1.5 inch id chemical hoses (Chemiflex) with polypropylene coated inner spirals, compared to a hose with a smooth bore (Coronado). The "smooth bore" hose data are enveloped by the least conservative Schon equation predictions, as discussed in Appendix E. However, the other hose data [7] are in excess of any published Schon equation predictions, even those allowing for pro-static agents. It can be seen that even at very low flow velocities, the charge densities are well in excess of the 20-30 $\mu C/m^3$ "hazard" levels established for tank truck filling and at higher velocities might approach the charge densities generated by filters. The effect of the spirals might be emphasized in small diameter hoses, owing to the greater blockage ratio. While such small hoses (less than 3 inch) are relatively uncommon in petroleum tanker operations they are not uncommon in the chemical industry, where toluene and other non-conductive products may be handled. The most important aspect of this high charging is that the hose might be the last component in a loading system and such hoses often go directly into the receiving tank with no relaxation volume at all.

Figure 5 : Charging in Smooth and Rough Bore Chemical Hoses



(4) Effect of Unbonded or Broken Inner Spiral

The following is a brief account of a toluene fire involving a conductive composite hose: The fire occurred as a toluene tank (8500 gallon aluminum) was bottom-unloaded through a composite chemical hose. The tank had been at the loading rack for at least an hour prior to unloading, which was carried out at 250 gpm. The fire was observed 5-7 seconds after the change in pump sound indicated the tank was empty. There was no explosion, but flame and black smoke came out of the tank manway. Fortunately, the mixture in the tank was sufficiently rich to allow the deflagration to be vented from the manway without overpressuring the tank. After the incident it was observed that the hose carcass was strongly charged and a spark was in fact produced on its outer surface. The charging was caused by the passage of toluene (a static accumulator) through the hose. The toluene became charged and static was deposited on the hose walls. The static was not drained away to ground.

The hose was a lightweight plastic type with both inner and outer metal spirals. The inner spiral was coated with an insulating plastic. After the accident, it was found that there was no continuity between the end connectors. The outer spiral was either broken or failed to make contact with at least one end connector. The inner spiral was isolated from both end connectors by a substantial gap (about 1 cm). This was inherent in the hose design, in which the inner spiral served only to form and strengthen the hose. Also, even had the inner spiral been connected at both ends, its plastic coating would have prevented dissipation of charge inside the hose to ground. It was subsequently found that other hose manufacturers had neglected the hazards of an

isolated inner spiral. A major problem is that if the external spiral is intact, resistance tests will not show whether an inner spiral is intact or bonded at the ends.

The probable cause of ignition was a spark from an isolated inner bonding spiral in a highly charged hose. While the hose was full of toluene, any sparking across the spark gap(s) to the end connectors (or other gaps) was of no significance because of the lack of oxygen (also, the presence of liquid toluene would increase the dielectric strength of any spark gap relative to a vapor and suppress sparking). When the toluene drained out, sparking would have occurred as soon as the liquid toluene was replaced by vapor, owing to the drop in dielectric strength. Evidently, the toluene-air mixture ignited and a flame propagated back to the tank.

This hazard exists only for flammable, non-conductive liquids during hose draining, when there is a vapor-air mixture formed in the hose.

Where such a hazard exists, hoses with semiconductive liners might be considered and are commercially available using carbon or metal-filled polyolefins. "Semiconductive" hoses made entirely of carbon black impregnated rubber are a less desirable option in cold climates since they become stiff and may crack.

Other solutions to the "unbonded inner spiral" problem involve means of checking continuity. One hose design uses a deliberately unbonded outer spiral and a bonded inner, ensuring that the status of the inner spiral can be checked. Other designs use bonding of both spirals, or this plus a semiconductive liner. The author has suggested that in order to both achieve end connector bonding and allow simple tests of inner spiral continuity, one might simply disconnect one end connection of the outer spiral while bonding the inner at both ends. The advantage of this over a completely unbonded outer spiral is that the latter would represent an ungrounded conductor. Bonding at one end would remove this possible spark hazard. These options are required in manufacture owing to the mechanical importance of the outer spiral and the need for careful inner spiral design if this is to be the means of bonding.

Lack of end connector bonding is more likely to pass unnoticed than inner spiral breakage, since the latter should soon cause visible hose collapse.

Rubber Boots on Fill Pipes

It was found in [33] that a semiconductive (5×10^8 Ω.m.) rubber boot on the end of a dip pipe greatly increased charging and was described as "potentially hazardous". Tests with a conductive rubber boot (2.3×10^4 Ω.m.) showed no significant charge generation. This suggests that intermediate and high resistivity boots should not be used for tanker filling.

API Velocity-Diameter Criterion for Tank Truck Filling

It is shown in Appendix F that for unlined metal container filling there is no significant static accumulation for conductive liquids and most semiconductive liquids. It is only necessary to limit the filling rate for non-conductive liquids and some semiconductive liquids which under field conditions might have effective conductivities of about 50 pS/m or less. Additional measures are required if filters are present. API RP2003 gives the following criteria for safe tank truck filling:

$$v \cdot d \leq 0.5$$

where v = flow velocity (m/s)
d = pipe diameter (m)

and $v < 7$ m/s

The only justification for the limit of 7 m/s is that it is outside of the range of test work conducted up to about 1976. In practical terms, loading velocities are normally less than 7 m/s.

Basis for Velocity-Diameter Criterion

Research by Shell [8,24, 31] is described in detail in Appendix F. In a series of papers it was concluded that:

(a) For the safe filling of road tankers with tank length ≤ 2 m, the velocity-diameter product should be limited to:

$v \cdot d \leq 0.50$ m^2/s for top filling

$v \cdot d \leq 0.36$ m^2/s for bottom filling (25% lower than for top filling)

For longer tanks:

$v \cdot d \leq 0.50 \cdot (L/2)^{0.5}$ for top filling

$v \cdot d \leq 0.36 \cdot (L/2)^{0.5}$ for bottom filling

For long compartments such as rail cars without baffle plates, a vd of about 0.6 m^2/s was acceptable. If the car has baffles, the length is defined by the baffle separation.
Hazardous discharges were not observed for charge densities below 30 μC/m^3 during overhead filling via a dip pipe and below 20 μC/m^3 during bottom connection filling.

(b) Splashing does not itself generate significant amounts of charge, although overhead filling pipes should be fully inserted as an additional safeguard to minimize their action as spark electrodes.

(c) Foam was not found to be a source of static discharges either from its surface or when conductive objects were buoyed up in it.

(d) "Sparking" could readily occur to roof projections as well as to a partly inserted pipe. There is no need to impose additional limits on loading rates in the early stages of filling ("slow start").

(e) Residence time downstream of microfilters should be 100 s.

(f) Precautions should be taken to avoid the presence of free water in the product and the severe blockage of wire mesh screens. The effect of free water was not examined in [31] for a truck filling system and the recommendation was conservatively based on earlier work with large tanks such as [1]. The latter point derives from [34] in which over 1000 $\mu C/m^3$ was produced by a 118 wire/cm strainer blocked with rust, and from [31] in which 350 $\mu C/m^3$ was produced by a 80 wire/cm strainer blocked with rust.

Research by British Petroleum [24] concluded that:

(a) For fuel with a conductivity greater than 10 pS/m no restrictions on flow rates are required except that the flow through a single loading point should never exceed 3500 liters/minute.

(b) For fuel with a conductivity between 5 and 10 pS/m the velocity-diameter product should not exceed 0.5 m^2/s.

(c) When the conductivity is less than 5 pS/m the velocity-diameter product should not exceed 0.36 m^2/s.

(d) A "slow start" is unnecessary provided the fuel is dry. If the fuel has more than 0.5% free water the initial velocity should be limited to 1 m/s until the filling pipe is submerged.

(e) The hazardous level of conductivity for tank truck filling is less than 10 pS/m and a survey of petroleum products showed that a quarter had conductivities less than this. It was suggested that antistatic additives raising the conductivity above 10 pS/m would solve the problem.

The conclusions (b-c) with respect to conductivity are difficult to put into practice owing to the non-constancy of conductivity (temperature and other effects). It was a major objective of the Shell work to avoid any conductivity dependence in their v•d product limit. The finding that 10 pS/m is a better "hazard" demarcation than 50 pS/m agrees with a Shell [8] finding that sparks were not observed above 4 pS/m. The apparent existence of this safety factor in taking action at 50 pS/m is significant in mitigating the "effective conductivity" effect (Appendix A) in which charged liquids display a much reduced (and unpredictable) conductivity when highly charged. The slow start criterion at 0.5% water is rather higher than that of 0.1% water recommended by Gibson and Lloyd [34] in a study involving toluene.

Research by PTB (Physikalisch-Technische Bundesanstalt) of Braunschweig, Germany led to a velocity-diameter limitation of 0.38 m^2/s for top loading of tank truck compartments [24,32]. This was considered valid provided that the filling pipe extends to the bottom of the tank, there is at least a 100 second residence time downstream of any microfilter, the product contains no free water or colloidal material, and the overall filling velocity does not exceed 7 m/s. For lengths between 2.8 m and 7 m the velocity-diameter limit should be:

$$v \cdot d \leq 0.23 \cdot L^{0.5}$$

where L = diagonal of midheight cross sectional area of tank (m)

Differences between these findings and those of Shell [31] arose principally because of different assumptions made about the maximum charge density arriving from the supply system.

A possible oversight in all the above research is that the filling was done by pipe. Additional charging by spiral wound chemical hoses with rough bores [7] or some types of flexible steel hose might make the recommended velocity-diameter criteria non-conservative in cases where such hoses are used. One company reports that they have replaced composite hoses with aluminum pipe for this reason.

Tank Truck Petroleum Distillate Filling Practices in the UK

A Petroleum Institute road tanker discussion meeting in 1979 [24] revealed the following current practices for operations in the UK:

EXXON: 400-500 igpm through 4 inch lines ($v \cdot d = 0.38 - 0.48$ m^2/s) with the flow restricted to 25% of this for the first 100 imperial gallons.

BP OIL: 500 igpm ($v \cdot d = 0.48$ m^2/s) through 4 inch lines.

MOBIL: 250-300 igpm through 3 inch lines ($v \cdot d = 0.32 - 0.38$ m^2/s) and 650 igpm through 6 inch lines ($v \cdot d = 0.41$ m^2/s), with both slow start and antistatic additives added to all middle distillate products.

TOTAL: 500 igpm through 4 inch lines ($v \cdot d = 0.48$ m^2/s) with initial slow start on arms used solely for middle distillate products.

TEXACO: 300 igpm through 3 inch lines ($v \cdot d = 0.38$ m^2/s) and 450 igpm through 4 inch lines ($v \cdot d = 0.43$ m^2/s), both with a slow opening valve which allows the first 70 gallons to be transferred at a flow velocity of 3 feet per second.

BURMAH: 500 igpm through 4 inch lines ($v \cdot d = 0.48$ m^2/s) with the first 100 gallons loaded at 100 igpm ($v \cdot d = 0.095$ m^2/s).

SHELL UK: 500 igpm through a 4 inch arm ($v \cdot d = 0.48$ m^2/s). A slow start was not used and had not been used for 25 years.

From this it can be seen that somewhat different practices had been evolved by different companies both in the maximum value of velocity-diameter and in the need for a slow start. By this time all of the experimental research on safe tanker filling described above had been published.

Fires at Low Values of Velocity-Diameter Product

A US company reported (private communication) two recent switch loading fires during bottom connection filling. In the first, mineral oil of conductivity about 2 pS/m was loaded into a 3000 gallon tank truck previously containing toluene. Filling was via a 4" spiral wound chemical hose with slow start of 100 gpm going to a cut-off maximum of 500 gpm. There were no unusual static generators in the filling circuit, and all ground connections had been properly made. At the time of the ignition, 1119 gallons had been loaded and the estimated flow rate was about 400 gpm. Thus, the velocity-diameter product varied between 0.08 and 0.39 m^2/s, with probable value of about 0.32 m^2/s at the time of the incident. The API velocity-diameter criterion of 0.5 m^2/s suggests that up to 625 gpm should have been safe for tank truck filling using a 4" loading arm. Whether this incident was caused by the spiral wound hose or jetting effects, or a combination of both, is unknown. It is noted in BS 5958 that bottom connection filling produces higher liquid surface potentials than top loading, because the grounded fill pipe is absent. It recommends that

flow rates be reduced to 25% of those for top loading unless there is an equivalent grounded fitting such as a dip tube, standpipe or baffle plate mounted centrally in the tank and reaching from top to bottom. The possibility of bottom connection filling is not considered in API RP 2003.

As reported in [24] two top filling tank truck loading incidents in the BP Rhur refinery occurred with a velocity-diameter product of 0.39 m^2/s (v = 2.6 m/s) and a fuel conductivity of 2.5 pS/m. There was no evidence of free water or strainer blockage. Another incident in Leeds, England in 1979 occurred when a road tanker was being filled with gas oil of 2.8 pS/m conductivity at no more than 500 igpm through a 4 inch line ($v \cdot d < 0.48$ m^2/s). This was a switch loading incident in which there were no filters or free water and only 60 mesh strainers present.

Tanker Fire Involving High Flash Point Liquid Mist

ICI [24] described the ignition of gas oil mist in the absence of switch loading, when a rail tanker was being splash filled at 1200 igpm through a six inch pipe ($v \cdot d = 0.76$ m^2/s). A short duration fire occurred when the tank was one-third full. As shown in Appendix C, the ignition energy of fine gas-oil mist approaches that of the vapor when the representative droplet diameter is less than about 30 microns. In [38] it was observed that fine diesel oil mist (representative diameter 7 μm) could be ignited by positive brush discharges at surface potentials above 60 kV. Ignition at lower potentials might well be possible for large liquid-to-wall discharges ("go devils") on the assumption that these should carry far more charge than brushes. Since this was a gas-oil (high flash point) tanker it was apparently not considered necessary to adhere to a velocity-diameter restriction.

Even at high flow rate the incident should have been avoided by bottom connection filling via a deflector, which would have greatly reduced the mist concentration. Very dense mist clouds are necessary to achieve the lower flammability limit of about 50 mg/liter throughout the vapor space, although this is readily exceeded close to the surface of a disrupting foam layer.

Tanker Fire(s) Involving Splash-Filling Conductive Liquid

Reference [52] describes a fire during butyl acrylate (FP = 50 C) splash-filling of a rail car containing methyl methacrylate (FP = 13 C) vapor from a previous lading. Pumping rate was 92 liters/sec through a 10 cm loading spout. Diagrams in [52] suggest that the deflector/thrust neutralizer at the bottom of the loading spout extended about two-thirds the way into the tank, and that the incident occurred when the tank was filled to about one-quarter of its height. The car had been flushed of liquid but not gas freed before filling. The tank was not inerted since oxygen is needed for acrylate polymerization inhibitor action. A suction vapor hose was in the open dome but no ignition source in the vapor line was identified. There was "absolutely no external ignition source within a reasonable distance". The paper [52] considered the ignition scenario to comprise the formation of a 0.5 m long liquid slug in a charged mist at a separation field gradient of at least 30 kV/m, followed by static discharge. The paper [52] stated that fields of 40-50 kV/m have been observed in this size of tank, referring to [2] for justification.

This author was unable to find justification for the "slug" mechanism in reference [2] or other work relating to such small tanks. Normally it is considered that the size of slugs and the electric fields produced by misting would be too small to yield the requisite stored energy. By comparison with conservative analyses made of marine chemical tankers with 3000 m^3 tanks, high velocity water washing does not produce hazardous "slug" conditions with a variety of chemical residues in the tank [53]. Since space potentials increase with tank cross-section and since the marine tanker tanks concerned are much larger than railcar tanks, for the "slug" mechanism to

have occurred in this case would suggest much larger space charge densities than have been observed.

Reference [54] describes experiments using high velocity sprays of water, acetone, toluene, xylene and mixtures which could contain solids. The experiments with single phases did not support the "slug" mechanism in tanks at least the size of road/rail transport tanks.

Paper [52] did not discuss whether the tank was lined or, indeed, whether the tank had become lined by an insulating layer of acrylate polymer. While acrylates will be inhibited to avoid hazardous polymerization runaways this might not prevent a slow surface accumulation of polymer especially since it is clear in this case that the cars were not completely cleaned after use. For highly conductive liquids one safety feature of a dip pipe is to deliver a continuous stream of liquid to the bottom of the tank. The conductivity of this stream then provides a ground path for small currents and polymer formation on the dip pipe itself is not a great concern. The company involved in the incident described in [52] privately reported to the author that in this case the tank was unlined and that they did not believe polymer had accumulated. The following mechanism might have been considered otherwise:

For a lined tank containing charged conductive liquid, there are two principal spark mechanisms. The first occurs as the liquid surface approaches a grounded surface such as the fill pipe, hose end connection or tank projection. The second is a liquid-to-liquid discharge as the liquid stream, initially above its break-up length, becomes continuous and forms a ground path. The spark in this case occurs between the charged liquid surface and the grounded stream of liquid impinging upon it. Initially a spark cannot occur because the stream breaks up into slugs and droplets before reaching the surface.

An order-of-magnitude calculation for tanks with insulating liners (Appendix H) indicates that the surface potential is proportional to the ratio of charge in the tank to the wall capacitance. Neglecting the tank end wall capacitances, the potential in a half-full tank will be given by:

$$\Phi = d \cdot S \cdot a / (4 \cdot \varepsilon_0 \cdot \varepsilon_r) \quad (V)$$

where

d	=	tank diameter	(m)
S	=	charge density	(C/m^3)
a	=	liner thickness	(m)
ε_r	=	dielectric constant of liner	

While an exact calculation could be made, the important point is that liquid surface potential is roughly proportional to tank diameter, charge density and liner thickness.

For a 2m diameter tank with 50 mil (1.27 mm) liner having a dielectric constant = 2, the potential in volts is about 36 times the charge density given in $\mu C/m^3$. For incendive sparks, a surface potential of a few kV will be needed to ignite most flammable vapors. These approximations indicate that significant charge densities, in combination with relatively thick insulating wall layers would be needed to give a hazard. High charge densities might arise from a deflector/thrust neutralizer considering in addition that a vapor extraction hose would remove fine droplets (which should carry a net charge opposite to that of coarse droplets and bulk liquid deposited in the tank).

There are few data for charge densities generated by conductive liquid spraying. Reference [54] used acetone ($\sigma = 5 \times 10^5$ pS/m) spraying at 50 bar from a 1.8 mm spray nozzle and found

250-300 $\mu C/m^3$ in the collected liquid. The charge densities were similar to that for water spraying from the same nozzle (250-750 $\mu C/m^3$). While the test conditions do not simulate the loading of tanks, these numbers support the general hypothesis that the spraying of conductive liquids into lined tanks might create hazardous surface potentials, particularly where rapid shear conditions exist at the nozzle (such as might occur in a deflector/thrust neutralizer).

For lined tanks it is clearly unadvisable to use filters at the bottom of loading circuits for conductive liquids, such as clamping a bag filter to the end of a hose or dip pipe. In this case significant surface potentials might arise prior to submersion of the grounded pipe.

Survey of Tanker Fires before 1979

An analysis of accidents with non-conductive liquids worldwide [24] indicated that prior to 1973 there were approximately 10 per annum and that between 1973 and 1976 there were approximately 6 per annum. 59% of the accidents were with splash filling, 72% were with switch loading and 84% involved one or other of these procedures.

Effect of Foam Production

In addition to the avoidance of splash filling, slow starts have been recommended partly to avoid foam production. It has been supposed [2] that foam accumulates charge and furthermore can give rise to incendive discharges, and Strawson [31] cites a paper in which foam was believed to be a common cause of tank truck explosions owing to the buoying up of loose metal objects inadvertantly left in the tank. However, large-scale research by Shell [31] showed no such behavior. Even at high inlet charge densities exceeding 300 $\mu C/m^3$, no unusually high charge was measured in the foam. Further, a large number of filling tests using metal objects (spheres ranging from 37-115 mm diameter and some rectangular plates) guided in various ways through the foam to wall-mounted targets gave no incendive discharges.

Foams of high flash-point liquids can readily be ignited by capacitance sparks. In [6] it was reported that diesel oil foam could readily be ignited by 2 mJ sparks and that the foam proceeded to burn slowly and erratically according to droplet size and concentration of the mist produced. However, brush discharges could not be made to ignite the foam even at liquid potentials up to 85 kV, regardless of electrode size and liquid polarity. It was observed that the foam was attracted towards the grounded electrode and that the foam tended to disperse the discharge over a larger volume. In [38] it was shown that ignition in a brush discharge must occur in the region close to the discharging electrode, where the greatest potential drop occurs. This region has the greatest power density and is visible as a highly luminous "root". It was observed that the root region of positive brush discharges could not be made to coincide with the foam surface owing to foam attraction towards the electrode. The small power density of the dispersed discharges produced in the presence of foam was insufficient to cause ignition. A major difference between brushes and capacitor discharges of equal energy is the low power density of the former. In order to ignite foam, it must first be vaporized. It is unproven that brush discharges are incendive towards foams of high flash-point liquids. The accidents that have been reported might have involved large surface-to-wall discharges similar to those seen during silo filling or a large ambient mist concentration caused by splashing, surging or a copious disrupting foam layer.

Baffle Plates

It is well known that grounded objects positioned above charged liquid surfaces can draw static discharges to themselves and that this is especially hazardous in the middle of large tanks and when the object has a radius of curvature of about one-quarter inch to an inch. Baffle plates may

have large openings in them, made by punching out the metal. This can leave a rounded edge which might perform as an effective electrode. It is prudent to avoid any rounded surface with radius of curvature more than about 2.5 mm. However, there is no infomation on this possible effect of baffle plates and it is known that "Go Devils", which appear as wall-to-surface discharges up to two feet long, may in any case develop at high levels of charging.

Safe Streaming Current Inference of Velocity-Diameter Limit

The inference from any velocity-diameter criterion is that there exists a maximum acceptable value of streaming current. This follows from equation E.2, viz:

$$I_S = \chi\, v^2\, d^2 \quad \text{amperes} \qquad \text{(E.2)}$$

or $$v \bullet d = (I_S / \chi)^{0.5}$$

where χ = empirical proportionality constant ($C.s.m.^{-4}$)

If $(v \bullet d)_{max} = 0.5$ the implied maximum acceptable streaming current (I_{max}) may be determined from (E.2) using various published values of the constant χ, as shown in Table 2.

Table 2 : Implied Maximum Acceptable Streaming Currents

χ ($C.s.m.^{-4}$)	Worker [Ref] Pipe or Hose Type	I_{max} (μA)
3.75×10^{-6}	Schon [22] : 1-8" pipe Britton [7] : smooth bore hose	0.94
9.42×10^{-6}	Strawson [4] : 4" pipe	2.36
25×10^{-6}	Britton [7] : 2" Pipe (Klinkenberg data)	6.25
87.4×10^{-6}	Britton [7] : 2" Rough Bore Hose	21.8

The latter two cases involved exceptional levels of charging produced in the first instance by the addition of a pro-static agent and in the second by the use of a spiral-wound hose of small diameter. Since the first two values of χ are held to cover most cases, it can be seen that a single velocity-diameter criterion of 0.5 m^2/s will not be 100% safe owing to the possible use of composite hoses and the presence of pro-static agents. Based on the incident analysis and the findings of BP and PTB, a safer limit for velocity-diameter is 0.36 - 0.38 m^2/s for top filling.

The analysis can be further extended as follows. If it is assumed that the Schon equation adequately envelopes streaming currents during the overhead filling cases studied by Shell, one can take 0.94 μA as the maximum acceptable streaming current (or 2.36 μA if the Strawson value for χ is used). To allow for the effect of pro-static agents (such as the Nasuleds corrosion inhibitor used by Klinkenberg), one would need to modify the v•d product:

$$v \bullet d = (I_S / \chi)^{0.5} = 0.19 - 0.31 \quad m^2/s$$

where I_S = 0.94 or 2.36 μA (maximum safe streaming current implied by Schon or Strawson)

χ = 25×10^{-6} C.s.m.$^{-4}$ (Klinkenberg data from Table 2)

This suggests that if pro-static agents are present the recommended v•d product should be reduced by 50% (for example from 0.50 to about 0.25 m^2/s).

Similarly, were a 2 inch spiral wound composite hose used (Britton data from Table 2), χ would be 87.4 μC.s.m.$^{-4}$ and the v•d product would be reduced to the range 0.10 - 0.16 m^2/s. Such low values of v•d product (about 0.13 m^2/s) would call for low flow rates that might be commercially impractical.

Effect of Pipe Diameter on Maximum Safe Flow Rate

The existence of a maximum velocity-diameter product for safe tanker filling implies that for fixed rates of filling a small diameter pipe is more hazardous. For some safe safe v•d product K:

$$v \cdot d < K \qquad (m^2 s^{-1})$$

Since flow rate

$$f = v \cdot A \qquad (m^3 s^{-1})$$

where A is the pipe cross sectional area, it follows that:

$$f < \pi \cdot K \cdot d / 4 \qquad (m^3 s^{-1})$$

So whatever value of K one adopts, one can use a proportionally larger flow rate with larger diameter pipes and still be safe. Conversely, a small pipe will raise the level of charging and furthermore compound the effects of turbulence and additional charging caused by internal spirals or other flow blockers in the hose.

Recommendations in BS 5958

This Standard is based largely on the Shell work [31] and recommends:

(1) Avoid splash filling. Use bottom loading or use a dip pipe that reaches to the bottom of the tank. Where filling is made through an open hatch without an internal fill pipe, the hose or loading arm should be inserted to the bottom of the tank without actually touching it.

(2) Avoid air or gas entrainment in liquids up to 50 pS/m conductivity where there is sediment or immiscible liquid in the tank bottom.

(The use of air eliminators is common practice. These contain rubber internals and there is no available study addressing whether these are static generators and should be placed some distance upstream of a tank. Experiments at Southampton University [33] showed that rubber boots designed to fit on the end of dip pipes generated significant static)

(3) For liquids of conductivity up to 50 pS/m the flow velocity should not exceed 1 m/s in the presence of a second immiscible phase such as free water. In the absence of a second immiscible phase the velocity should not exceed 7 m/s.

(4) For liquids of conductivity above 5 pS/m the velocity-diameter product for top filling should not exceed 0.5 m^2/s. The product is calculated based on the diameter of the smallest upstream pipe run except where (i) the run is less than 10 m and (ii), the diameter is not less than two-thirds that of the next larger run. If these two conditions are met the diameter of the next larger pipe run can be used.

(5) For liquids of conductivity less than 5 pS/m a velocity-diameter product of 0.5 m^2/s is used in the UK although a value of 0.38 m^2/s has also been accepted.

(6) Special cases are allowed for tanks or compartments longer than 2 m. If the velocity-diameter limit is calculated as above, the calculated flow rate can be increased by a factor of $\sqrt{(L/2)}$ for lengths between 2 - 4.5 m and by a factor of 1.5 for lengths above 4.5 m provided that the upper limiting velocity of 7 m/s is not exceeded.

(7) For bottom loading the flow rates should be 25% less than those calculated for top loading unless there is a grounded body mounted centrally across the height of the tank (baffle plate, standpipe or dip tube) to compensate for the absence of the top filling dip tube.

GENERATION OF STATIC IN FILTERS

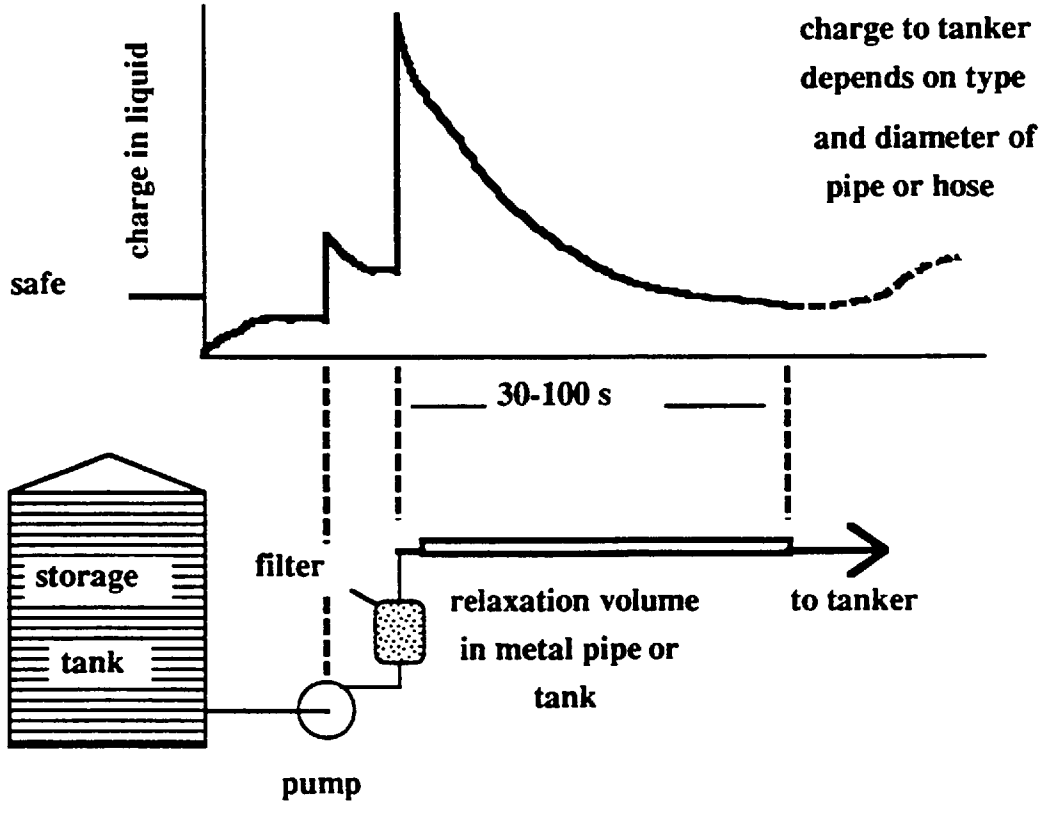
Theory and Experiment

The theory and experimental findings for charging in various types of filtration device are presented in Appendix F. Existing theories are inadequate for quantitative predictions of either magnitude or sign of charge density leaving the filter device. Changes in filter material, and very small changes in the type and concentration of contaminants in the liquid can greatly change both magnitude and polarity of charge.

The filter material has a significant but unpredictable effect on the magnitude and polarity of charge. Not only the more common filters (paper, clay, textile) but also filters made of metal sinters [47,48] can give high levels of charge.

Experimentally it is shown that a microfilter (nominal pore size less than 50 microns) can transiently increase the charge density by up to about 3 orders of magnitude relative to flow in smooth pipes. Whereas the charge density in pipe flow is roughly proportional to flow velocity, the charge densities produced by filters can be roughly independent of flow velocity, and in some cases may actually decrease with increased velocity [7, 43]. The charge density varies enormously with small amounts of ionizable contaminants but little correlation is found between charging and conductivity for non-conductive liquids [37, 43].

Figure 6 : Filter Charging Schematic



Large Container Filling

A microfilter should be placed a sufficient distance upstream of a container for transient high levels of charge produced by it to relax back to the steady-state "smooth pipe" value as shown in Figure 6. If sufficient relaxation time is not provided between the filter and the receiver, very high levels of charge can be introduced from the filling line. Eichel [57] describes the following observations by Shell Oil Co. made in 1963 during loading of filtered kerosene-type aviation fuel onto tank trucks at night:

"A crackling noise was heard and sparks up to 2 ft. in length were observed inside the tank. Fortunately the atmosphere inside the tank compartments was non-explosive. They had previously contained gasoline but had been flushed. All equipment was thoroughly grounded."

Subsequent investigation showed that the appearance and intensity of discharges depended on flow rate and therefore had an inverse dependence on relaxation (residence) time downstream of the filter. When the filter was bypassed no discharge phenomena were observed. Some of the tabulated observations were:

		Observations	
Flow Rate (gpm)	Relaxation Time (s)	σ = 0.5 pS/m	σ = 0.84 pS/m
100	63.5	none	none
200	31.7	none	none
300	21.2	none	none
350	18.1	corona	none
400	15.9	sparking	none
450	14.1	severe sparking	none
500	12.7	n/a	none
600	10.6	n/a	corona

Corona was defined as a pinpoint of bluish light on metal projections above the product level inside truck compartments. These points of light could be transferred to the fingertips when contacted with the bare hand. Minor sparking was defined as lightning-like flashes under 1 inch in length while severe sparking referred to flashes up to 24 inches long; the latter generally commenced when the compartment was two-thirds filled. As discusssed below, the effect of conductivity might have been enhanced by changes in liquid relaxation behavior in the region around 1 pS/m.

Since this was not a definitive study it is not a basis for determining safe filter location. The levels of charge encountered might be very much greater using different filters and test liquids. It did however define the problem, showed the importance of relaxation time and conductivity, and indicated that safe relaxation times must be at least 20 seconds.

For large tank (such as tank truck) filling, NFPA 77 and API 2003 call for a global 30 seconds relaxation time whenever a liquid with conductivity below 50 pS/m is involved. The figure of 50 pS/m was originally suggested in the 1950s [1, p. 138]. BS 5958 suggests 3 time constants for liquids with conductivity down to 2 pS/m and a global 100 seconds relaxation time for liquids of lower conductivity (this allows for non-exponential relaxation rates at very low values of conductivity). In practice, for flow velocities of 1-10 feet/sec, pipes or hoses of 100-1000 feet would be provided for downstream of the filter by the BS 5958 Standard under the very low conductivity provisions. Under US Guideline provisions (NFPA and API), hoses of 30-300 feet would be needed for these flow velocities. A relaxation tank has been suggested to provide the required volume downstream of a filter; alternatives are to employ a large diameter pipe or hose

plus a low flow rate, use antistatic additives or neutralizing devices, or inert the tank. As shown in Figure 6, it is important that the final pipe and hose connections at the loading rack be designed to meet v•d limitations, electrical continuity if swivel joints are present, and be internally as smooth as practicable.

Comparison of API and British Standard Provisions

In view of the variability of conductivity due to purity, temperature and excess charge, the provision for three relaxation times in BS 5958 offers no greater precision than API's use of a global 30 seconds for liquids of less than 50 pS/m conductivity. However, for conductivities of 1-2 pS/m or less, where liquids relax hyperbolically, it is shown in Appendix A that about 100 seconds of relaxation is required to reduce excess charge to acceptable levels, and this is recommended in BS 5958. Although charging is often much reduced for liquids of such low conductivity, this is compensated for by the fact that the time for charge dissipation to a safe level is practically independent of the magnitude of initial charge density. If less charge is generated, the presence of a charge density term in the hyperbolic relaxation rate equation means that the charge will take longer to dissipate. The research of Shell and PTB also conclude that 100 seconds relaxation time is needed for very low conductivity liquids.

Need for 100 Seconds Relaxation at Low Conductivity

Experimental data by Bustin [2] also show that a global 30 seconds relaxation time is not safe. The tests compared the charge density leaving a microfilter in an 8 inch pipe to that remaining 30 seconds downstream, using liquid of rest conductivity in the range 0.01 - 2.2 pS/m. The following table lists and analyses the experimental results. It can be seen that in several cases the charge density remaining after 30 seconds "S_{30}" was greatly above the hazardous threshold (20 - 30 $\mu C/m^3$). In the final column, it can be seen that the errors in assumption of exponential (EXP) relaxation switch from positive to negative at a conductivity around 1 - 2 pS/m, whereas the hyperbolic (HYP) model (assuming $\varepsilon_r = 2.0$ and $\mu = 1 \times 10^{-8}\ m^2V^{-1}s^{-1}$) gave agreement which may have been within experimental measurement errors.

Table 3 : Analysis of Charging and Discharging During Filter Flow

σ (pS/m)	S_0 ($\mu C/m^3$)	S_{30} ($\mu C/m^3$)	% Left (Measured)	% Left (Predicted)	
				HYP	EXP
0.0167	64.6	32.3	50	47.7	97.5
0.0205	78.2	41.4	53	43.0	97.0
0.0223	78.0	30.4	39	43.1	96.7
0.0252	75.5	28.7	38	43.9	96.3
0.0980	60.9	26.2	43	49.2	86.3
0.130	65.3	21.5	33	47.5	82.3
0.247	253	70.8	28	18.9	69.0
0.305	188	54.5	29	23.9	63.3
2.07	332	33.2	10	15.1	4.48
2.21	257	42.1	16.4	18.7	3.68

Small Container Filling

Clearly, relaxation time provisions developed for containers the size of tank trucks would have severe practical limitations for a drum filling operation, which might involve a range of quite different liquids. NFPA 77 recognizes this in recommending that the relaxation time be made as

large as practicable (there is far less risk of hazardous static accumulation in containers of drum size as opposed to tank trucks, but accidents due to close-coupled filters [6] have occurred).

Microfilters in Conductive and Semiconductive Liquid Service

For conductive liquids, no Standard or Guideline requires any relaxation time downstream of a filter. These liquids all have conductivities above 10000 pS/m, excluding them from NFPA and API. By the BS 5958 "three relaxation times" provision, Appendix B shows that this amounts only to milliseconds of relaxation. Semiconductive liquids can usually be excluded, but if their nominal conductivities are less than a few hundred pS/m the effect of temperature reduction in lowering conductivity (Appendix A) should be considered. This could make it hazardous to place a microfilter too close to a tank entry, but the required relaxation time should not introduce practical difficulties. Mounting of filters on the lower ends of dip pipes and hoses should not be carried out for some semiconductive liquids. This arrangement would provide no relaxation time and might be especially hazardous in lined tanks during the early stages of filling. No data are available to assess the actual hazard.

GENERATION OF STATIC DURING SETTLING AND STIRRING

Enhanced electrification can occur during relative movement of solids or insoluble liquid droplets in a non-conductive continuous liquid phase. Examples include stirred slurries, water droplets settling in a tank of gasoline and the pumping of non-conductive liquids containing free water. Electrification occurs due to shearing of the double layer produced at the surface of the discontinuous phase.

Settling Potential

Klinkenberg [1] considered a dilute dispersion of equally charged solid spheres settling according to Stoke's Law in a quiescent liquid with very low conductivity (~1 pS/m). It is assumed that each droplet has a thick double layer surrounding it and transports a net charge to the bottom of the container, leaving a net countercharge in the bulk liquid. As a result a "settling potential" appears at the liquid surface. The following derivation is for the electric field in the liquid.

The force acting downwards on a particle (or droplet) is:

$$F\downarrow = \{4 \cdot \pi \cdot a^3 \cdot g \cdot (\rho_1 - \rho_2) / 3\} + Q \cdot E$$

where
- a = particle radius (m)
- g = acceleration due to gravity ($m.s^{-2}$)
- ρ_1 = density of particle (kg / m^3)
- ρ_2 = density of liquid (kg / m^3)
- Q = charge on particle (C)
- E = electric field (V/m)

From Stoke's Law the particle terminal velocity :

$$v = F\downarrow / (6 \cdot \pi \cdot \eta \cdot a)$$

where η = liquid viscosity (kg / m-s)

The current density due to "n" falling particles plus a contribution from conduction:

$$J = v \cdot n \cdot Q + \sigma \cdot E$$

where $\sigma \cdot E$ = conduction current

At an electrically steady state, if there is no current leaving the system:

$$0 = v \cdot n \cdot Q + \sigma \cdot E$$

If "X" is defined as the volume fraction occupied by the particles:

$$X = 4 \cdot \pi \cdot a^3 \cdot n / 3$$

Rearranging for "E" one obtains:

$$E = - Q \cdot X \cdot g \cdot (\rho_1 - \rho_2) / (6 \cdot \pi \cdot \eta \cdot a \cdot \sigma \cdot \alpha)$$

where α = ratio of uncharged particle settling velocity : charged particle settling velocity

$$\alpha = 1 + n \cdot Q^2 / (6 \cdot \pi \cdot \eta \cdot a \cdot \sigma)$$

For thick double layers (see Appendix E) the charge "Q" can be related to the zeta potential "ζ" using the expression for capacitance of a charged sphere:

$$Q = 4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot a \cdot \zeta$$

Hence

$$E = - (2 / 3) \cdot (\varepsilon_0 \varepsilon_r / \sigma) \cdot \{X \cdot g \cdot (\rho_1 - \rho_2) \cdot \zeta / (\alpha \cdot \eta)\}$$

$$\alpha = 1 + (2 \cdot X \cdot \sigma / \eta) \cdot \{(\varepsilon_0 \cdot \varepsilon_r \cdot \zeta / (\sigma \cdot a)\}^2$$

The inclusion of the "α" term in the expression for E indicates that the force exerted by the electric field on the particles reduces the settling velocity and consequently the final field strength. The factor (2 / 3) may change according to the double layer thickness [1]. For thick layers the constant is always (2 / 3), but for thin double layers the value varies from 1 for particles that are relatively non-conductive, to (2 / 3) for equal liquid and particle conductivity, to zero for relatively conductive particles. In the latter case, water falling through an oil will give zero electric field at high values of oil conductivity which will yield thin double layers. The theory should apply to settling of a few percent by volume of water in oil, provided that the tank has a large diameter-to fill ratio, which provides an approximation to zero current loss from the system.

Klinkenberg [1] worked an example for oil pumping in which 100 micron droplets are present at a volume fraction of 5%:

ε_r	=	2
ζ	=	0.025 V
X	=	0.05
g	=	10 $m.s^{-2}$
$(\rho_1 - \rho_2)$	=	300 kg/m^3
η	=	0.0005 kg/m-s (0.5 centipoise)
σ	=	1×10^{-12} S/m (1 pS/m)
a	=	5×10^{-5} m (50 micron radius)

Substitution in the equation for "α" ($\alpha = 1.016$) the electric field in the liquid is found to be - 90 kV/m, showing that large fields might be possible as small droplets settle. For much larger droplets, settling will be so fast that X and therefore E will quickly diminish. For much smaller droplets, the factor "α" will increase and E will decrease. In [1] this effect is described as a haze which floats in the electric field the constituent particles are producing themselves, and large fields are not attained. The settling potential at the surface of the liquid is given by {E•h}, where "h" is the filling depth. If the tank has a total height "H", the field in the vapor space is {E•h / (H - h)}.

Liquids Plus Solids : Stirred Slurries

There is limited information on the hazards involved with stirred slurries. Vos et al. [82] discussed a flash fire caused by stirring epoxy resin into xylene of conductivity about 50 pS/m. There were no operators near the blender and the conductivity level was too high for charging via simple agitation of the liquid. It was clear that the rate of charge generation was such as to overcome the charge relaxation. Experimental work showed that the charge density increased with stirrer speed and that the chemical composition of the solid phase was less important than particle size. Both organic and inorganic solids caused high charge densities.

The preferential adsorption of ions from the liquid causes the particles to become charged with surrounding countercharges which can be sheared due to the velocity gradient. The counter-ions thus become separated from the particle and its electric field, explaining the formation of the separate charges.

Increased stirrer speed (or power input) increased charge density rapidly until a maximum was attained. There was found to be an optimum particle size for charge generation, believed due to an optimum combination of high surface area and high velocity gradient between the particles and the liquid. Thus, large particles (~4 mm) have a low surface area and also tend to sink to the bottom of the vessel, while small particles (< 0.3 mm) have a small settling velocity and tend to float through the liquid phase. Particles of intermediate size have a relatively high surface area plus a sufficient settling velocity to give surface shear effects; charge densities as high as 450 $\mu C/m^3$ were measured in the test apparatus. The charge density decreased fairly linearly with increased temperature in the range 20-100°C, amounting to about 5% per degree Celsius.

It was found that addition of polar solvent or antistatic additive initially increased charge density despite the elevation of conductivity. To reduce the charge density to 10 $\mu C/m^3$ it was necessary to increase conductivity to 2000 pS/m, such as by adding up to 10 vol% of a polar solvent to the xylene. Large scale tests indicated that 1000 pS/m conductivity would reduce the charge density to about 10 $\mu C/m^3$, which was similar or less than that obtained with xylene alone.

CHARGE GENERATION IN JETS AND SPRAYS

During mechanical disruption of liquids such as spraying, a type of charging sometimes referred to as "balloelectric" charging occurs. This is observed with liquids of all conductivities including water.

Rayleigh Limit

The maximum charge that can be held by an isolated droplet is limited by the condition that repulsive forces due to the charge will eventually balance the surface tension force holding the surface together. Above this limit the droplet divests excess charge by deforming, disrupting and spraying off the excess charge. The theoretical limit is given by:

$$Q = 8 \cdot \pi \cdot (\varepsilon_o \cdot \gamma)^{0.5} \cdot a^3 / 3$$

where Q = charge (C)
γ = surface tension coefficient ($N.m^{-4}$)
a = particle radius (m)

Field and Potential Effects of Space Charge

Appendix H shows derivations of fields and potentials in grounded containers containing homogeneous space charge. These are applicable to containers containing charged mist such as created during tank washing.

Field at Grounded Projection or Fieldmeter

van de Weerd [55] considered a grounded spherical probe of radius "r" at the center of a sphere of radius "R" containing charged mist of charge density "S", where R >> r. For practical purposes, the field at the surface of the probe E_r is given approximately by:

$$E_r = S \cdot R^2 / (6 \cdot \varepsilon_o \cdot r)$$

This expression is numerically equal to the maximum space potential without the probe present, which occurs at the center of the spherical container. Hence, if an electric fieldmeter is lowered into a tank containing charged mist, the maximum tank potential that would be exerted in the absence of the fieldmeter should be directly related to the measured electric field. In practice, an adjustment is required to the measured field to allow for the actual geometry. Chubb [56] gives this as 11 kV/m per kV, for an approximately cylindrical fieldmeter head 90 mm in diameter.

Without the probe present the maximum field is exerted at the wall of the spherical container (E_w) and is given by:

$$E_w = S \cdot R / (3 \cdot \varepsilon_o)$$

Hence the maximum field with the probe present is magnified by a factor:

$$E_r / E_w = R / (2 \cdot r)$$

The onset of discharges in the container will therefore be dominated by the effect of projections in the charged mist.

Tank Cleaning with Water Jets

The formation of charged mist during tank cleaning has been reviewed by Barreto [83]. Water molecules are by nature permanent dipoles. In the bulk material thermal agitation keeps these dipoles randomly oriented. However at the air-water interface this effect is reduced and it is estimated that about 1 in 30 molecules is selectively oriented with its positive end towards the water. Even pure water contains free ions by dissociation, so the positive ends attract negative ions to the surface from the water bulk. Since dipoles themselves carry no net charge these negative ions form a net negative charge layer just beneath the surface, while thermal agitation prevents formation of a positive neutralizing layer below this. For pure water it is estimated that there is one negative ion for each 10^4-10^5 water molecules at the surface in a layer about 8×10^{-9} m thick. At the air-water interface there are about 10^{19} molecules per square meter.

During rapid shear processes such as splashing and spraying, very thin filaments and films are formed having thicknesses of the same order as the charged surface layer. Fine mist formed from such filaments and films thus carry a net negative charge while coarser droplets formed from the bulk liquid carry a positive charge. As the coarse droplets settle out of suspension the mist left behind has a negative charge.

In practice impurities from the water and tank walls may affect this simple description of the charging process. This may involve surface tension changes and changes in the ions present. Sea water, for example, usually creates a positively charged mist.

The charge density found experimentally in the mist created during high pressure water washing of tanks is of the order 10^{-8} to 10^{-7} C/m^3 and does not represent a hazard in most tanks including barge tanks. The loss of three supertankers was attributed to sparks produced from slugs of water traveling through charged mist contained in enormous center tanks, where space potentials could attain 30 kV or more. In smaller tanks such as on barges, such large space potentials are not attained unless live steam is introduced during the hot wash cycle. This can occur during start-up or poor control of steam injector systems and may be avoided using a hot water tank. Other differences in smaller tanks are that the wash nozzle diameter is smaller than those used on supertankers, there are few (if any) complex internals from which water can drain, and the jet travel distance is smaller. These considerations plus the fact that choppy seas will not be throwing up water heels make it unlikely that water slugs of any significant size (or capacitance) will form.

Steaming

Liquid Chemical Jets

Charging studies were made by Lundquist et al. with application to airless spray painting [49].

ACCUMULATION OF STATIC

Definitions of Conductive, Antistatic and Non-Conductive Grounding Terminations

Final termination of grounding buses or other systems must comprise a good earth ground such as a buried plate, driven rod, or underground metal pipe. Structural steel building frames which are effectively grounded, particularly when designed for lightning protection, are suitable. Semi-permanent connections of the bus or other termination should result in a ground resistance of less than 10 ohms according to BS 5958, or 25 ohms in [46], or other small value much less than the 10^6 ohms needed for simple static dissipation (see below). This is because greater values are indicative of poor connections which might fail altogether. As described in [46] underground piping equipped with cathodic protection is unsuitable as a termination, owing to the possibility of stray currents. Also unsuitable are underground piping systems with non-conductive sections or which might be disconnected for repair or alterations. Reference [46] recommends that sprinkler piping and electrical conduit also be avoided owing to the presence of joints and connectors, plus the likelihood of interruption for maintenance or alterations. Equipment such as water meters in piping should be jumpered.

Accumulation on Conductors

The capacitor "C" in Figure 7 represents a conductor (for example, plant equipment or a tanker) being simultaneously charged by a current (for example a streaming current) "I_S" and discharged by a leakage current "I_L" flowing through some parallel resistive path to ground. The charge "Q_t" on the capacitor at any time "t" is given by the equation for a "leaky capacitor":

$$Q_t = (C \cdot I_S \cdot R_L) \{1 - \exp(-t / R_L \cdot C)\}$$

The leakage current varies with time according to:

$$I_L = I_S \{1 - \exp(-t / R_L \cdot C)\}$$

When the capacitor is fully charged it implies that $I_L = I_S$. At this time the capacitor is at its maximum charge Q_{max} and potential ϕ_{max}:

$$Q_{max} = I_S \cdot R_L \cdot C$$

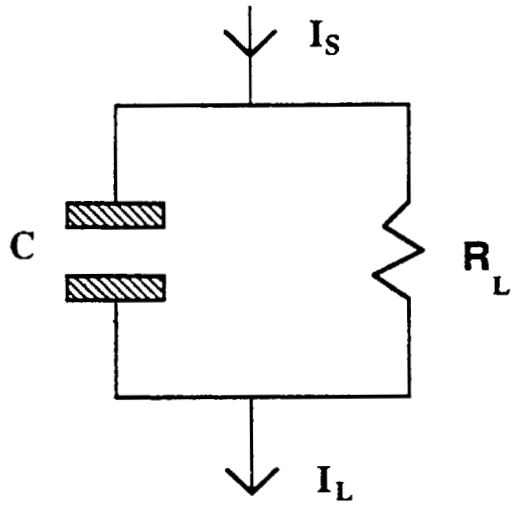
$$\phi_{max} = I_S \cdot R_L$$

The maximum stored energy W_{max} is given by:

$$W_{max} = 0.5 \cdot Q_{max} \cdot \phi_{max} = I_S^2 \cdot R_L^2 \cdot C / 2$$

Often the charging process will be limited by a parallel spark gap which will break down at a potential less than or equal to ϕ_{max}.

Figure 7 : Equivalent Circuit for Constant Current Charging



Grounding Criteria

With reference to Figure 7, the criterion for setting an acceptable value of R_L should ensure that even with the assumption of the highest practical value of I_S the maximum system potential cannot give rise to an incendive spark. There are two basic considerations:

(1) The maximum current I_S observed in liquid transfer systems (such as if a filter is present) is of the order 10^{-4} amperes. Currents are typically of the order 10^{-6} amperes or less.

(2) Owing to quenching distance considerations there is a minimum potential at which a static "capacitance" spark may ignite a gas mixture. Often the literature has made reference to the "quenching distance" which is based on flame propagation between electrodes fitted with large parallel guard plates around their tips. This has led to the misconception that about 1500 volts or more is needed for gas ignition; it is quite possible that a spark might originate between pointed electrodes, in which case the "flanged electrode quenching distance" is not a valid consideration.

As shown in [25], the ignition energy of diethyl ether is only about 2 mJ (only moderate quenching effects) using pointed electrodes at 1000 V potential. While in the same reference it is shown that the minimum sparking potential in ambient air is approximately 300 volts at a spacing of 7.5 microns, low voltage capacitance spark ignition can occur at voltages as low as about 10 V depending upon the gas and the capacitance involved, provided some form of make or break contact occurs. The largest items of plant equipment have a capacitance of about 10000 pF. At this capacitance hydrogen in air has been ignited at about 100 V while other gases tested (methanol or methane in air) required more than 800 V. To cover the cases of low ignition energy and relatively large capacitances, a conservative ϕ_{max} of 100 V might be used. This can be increased to at least 1000 volts for smaller capacitances (less than 150 pF) as shown in Appendix C.

Even with the conservative criterion of 100 V, a leakage resistance R_L of 10^6 ohm is satisfactory for grounding of static electricity, since if $\phi_{max} = I_S \cdot R_L = 100$ volts, this is satisfied at $R_L = 10^6$ ohm for a current as high as 10^{-4} amperes. In the absence of any prolific charge generator such as

a filter, and if only common solvent or hydrocarbon vapors (MIE ~ 0.2 mJ) are considered, the grounding requirement may be safely relaxed to about 10^8 ohm.

An alternative approach may be used to set higher acceptable ground resistances. If the capacitance is known and the current I_S can be estimated, the resistance can be selected so that the maximum stored energy is lower than the ignition energy of the gas or vapor mixture in question:

$$R_L = \{2 \cdot W_{ign} / (C \cdot I_S^2)\}^{0.5}$$

where W_{ign} = ignition energy of gas or vapor (Joule)

Accumulation on Non-Conductors

Static accumulation on non-conductors usually occurs by a streaming current into containers, relaxation of charge in pipes or in-situ generation by tribocharging. Other mechanisms include deposition by corona or (less important) polarization and dielectric absorption processes.

Provided the charge generation rate exceeds the rate of charge dissipation, the total accumulation is limited by electrical breakdown. This may involve breakdown of the liquid involved, the gas phase or the non-conductor itself. A special case involves a conductive surface coated with a non-conductor, such as a charged sheet of plastic in contact with a sheet of metal. In this case, the electric field has almost no air component for thin plastic layers and the field is exerted through the plastic to the metal substrate. As the plastic is made thicker, the air component of the field becomes significant. At moderate thicknesses, brush discharges can be produced above the charged plastic by introducing an electrode. However, for thin layers, no brush discharges are produced; instead, very high charge densities can be supported by the plastic, limited only by its breakdown strength (typically about 400 volts/mil). If the system is perturbed, such as by striking the plastic surface or introducing an electrode above it, massive electrical breakdown in the form of a "propagating brush" discharge can be produced. These cases are discussed in Appendices G and H.

Rubber Tyres : Charging and Resistance to Ground

Bulgin [68] showed that the electrostatic charge caused by separation of the non-conductive tyre treads from the pavement can raise a tank truck potential up to 100 kV, depending on road surface roughness, vehicle speed and tyre tread resistance. This typically occurs on dry roads when the tyre treads have a resistivity of 10^8 - 10^{11} Ω-m. When the road surface is a good insulator, for example, asphalt in dry weather, both the tank truck and the road surface can retain high potentials for significant periods after the truck has stopped. It was shown that lowering the tyre resistance from the typical 10^9 - 10^{12} Ω to below 10^9 Ω avoids the hazard of high truck potentials. "Non-static" tyres were shown both to decrease the peak potential on the truck and increase the rate of charge dissipation once the truck came to rest.

Mancini [70] gave ground resistances for a small van with four tread 4 polyester, 2 nylon ply tyres (sidewall 6 polyester plies) showing the effect of ground surface. Either resistance to an aluminum plate or to a nearby fire water line was measured at a source potential of 50 V. The weather was clear and dry (73 F, 41% RH) with no rain for four days. Results were:

Surface	Resistance (Ohms)
aluminum plate (one tyre)	4×10^8
concrete	5×10^8
asphalt	2×10^{10}
grass	4×10^7
clay/gravel - hard packed	3×10^8

The results showed that with the tyre used all the ground resistances would be less than 10^8 ohms except on dry asphalt. The decay time constant from an initial 300 V on the van was much less than 1 second except in the case of dry asphalt (several seconds). For a tank truck with typically about a dozen tyres Mancini concluded that the resistance would be about one-third of those measured and that grounding of the truck was primarily dependent on ground surface except where independent bonding/grounding is carried out.

Criteria for Assessing Charge Accumulation Hazards on Non-Conductors

High resistivity materials such as thermoplastics usually have volume resistivities in the range 10^{15}-10^{18} ohm-m but their surface resistivities may be much lower owing to contamination by water, dirt or topical antistatic agents. Normally, charge will bleed off the surface of non-conductors faster than through the bulk and common tests for "antistatic" plastics involve surface resistivity or relaxation time measurement.

Test methods are given in NFPA 99 and MIL-SPEC B-81705B.

Paint

In [49] a variety of solvent-based paints were applied as thin layers on metals and the thicknesses, resistances and resistivities measured before and after drying. For wet paint the resistivities were of the order 10^4 - 10^7 Ω-m and the layers could be considered conductive. For dry paint the resistivities were found to be in the range 10^{14} - 10^{15} Ω-m; the resistances for layers less than 1 mm thick were in the range 10^{11} - 10^{14} ohm. All of the dried paints were non-conductive and could hinder proper grounding of metals. Under certain conditions, high resistivity paint coatings might accumulate hazardous levels of surface charge.

Liquid Phase Charge Accumulation in Tanks

For liquid flowing into a conductive tank the charge "Q_t" and charge density "S_t" remaining at any time is given approximately by the "leaky capacitor" equation:

$$Q_t = I_S \cdot R_L \cdot C \{1 - \exp. (-t / R_L C)\}$$

since $\tau = R_L \cdot C = \varepsilon_o \cdot \varepsilon_r / \sigma$ (relaxation time constant)

and $S = Q / V$

then $S_t = (I_S \cdot \tau / V) \cdot \{1 - \exp (-t / \tau)\}$ (C/m^3)

where I_S = streaming current to tank (amperes)

$$V = \text{volume of tank} \qquad (m^3)$$

Complications are that in practice V is not constant as a tank is being filled, and if the tank is filled, some of the charge will flow out as it is displaced by incoming flow. However, the approximate relation holds fairly well for partly filled tanks provided the contents are well stirred. The streaming current to the tank I_S can be expressed in terms of flow rate f (m^3/s) and incoming charge density S_o:

$$S_t = (S_o \cdot f \cdot \tau / V) \{1 - \exp(-t / \tau)\}$$

For a typical hydrocarbon with $\varepsilon_r = 2$, substitution can be made for the relaxation time constant $\tau \sim 18 / \sigma$ where σ is given in pS/m. For a large tank in which the filling time t is much longer than τ, the expression reduces to:

$$S_t = S_o \cdot f \cdot \tau / V \sim 18 \cdot S_o \cdot f / (V \cdot \sigma)$$

These equations show that for conductive liquids the charge accumulation is negligible. If we set the inlet charge density S_o at the very high value of 5000 $\mu C/m^3$ and allow a tank to be filled in the very short time of one minute ($V / f = 60$ s), we have:

$$S_t = 5000 \cdot \tau / 60 \quad \mu C/m^3$$

From Appendix B, conductive liquids have τ values less than 10^{-3} seconds, giving negligible charge densities during filling. Semiconductive liquids have τ values ranging from about 0.4 seconds down to about 10^{-3} seconds, and only barely represent a hazard at the highest value of τ. For grounded, unlined tanks only non-conductive liquids with conductivities less than about 50 pS/m will normally accumulate hazardous charge densities.

Use of Antistatic Additives

A project begun in the 1950s [1] set out to develop additives that at concentrations of the order 10 ppm would increase the conductivity of hydrocarbons to several hundred pS/m. The need for effectiveness at low concentration is due to quality impairment and cost. The workers found, importantly, that synergistic effects occurred when combinations of electrolytes were used; much greater increases in conductivity could be obtained for mixtures than for the single component additives. A more or less empirical search for an optimum additive blend resulted in several conclusions [1]:

- o One component must be a divalent or polyvalent metal salt. Substituted salicylic salts compared favorably with other acid salts.
- o The other component must be an electrolyte which by itself imparts a conductivity of at least 10^4 pS/m to benzene as a 0.1% solution. It may also be a metal salt but should not have the same cation as the first component. Numerous candidates included salts of sulphonic acids.
- o The interaction of the components should be such as to produce a low charging effect.

Shell's additive ASA-3 is a dark, viscous mixture of equal parts of chromium dialkyl salicylate, calcium didecyl sulfo-succinate, and a co-polymer of lauryl methacrylate and methyl vinyl pyridine, supplied at 50% solids in a hydrocarbon. Competitive additives include Mobil's Stadis-3.

Problems of Additives in Practical Systems

Bustin [2] reviews the following problems experienced particularly in aircraft fueling systems:

- Depletion of additive in pipelines or (especially) in filters and filter-coalescers. This problem was offset by the good US accident record for Jet A which made the use of antistatic additives rare, and abroad by the low use frequency of clay filters.

- Effect of surfactant properties of additives on efficiency of water coalescers. This has been offset by new coalescer design.

- Potential for over-dosing of additive and its effect on aircraft capacitance-type fuel gauges that are sensitive to fuel conductivity. This can be offset by making spot conductivity measurements in the field.

- Potential for under-dosing to less than about 10 pS/m with attendant pro-static agent effects rather than anti-static effects which occur at higher conductivity owing to the dominance of charge relaxation. Again this can be offset by measurements of conductivity in the field.

STATIC DISCHARGES

Sparks

Most static sparks occur between conductors and are simple capacitance discharges (negligible inductive elements) with stored energy "W" given by:

$$W = 0.5\, C\, \phi^2 = 0.5\, Q\, \phi$$

where
- W = spark energy (Joule)
- C = capacitance of system (Farad)
- ϕ = potential difference across capacitor (Volt)
- Q = charge held by capacitor (Coulomb)

The capacitor can be any ungrounded conductor including a person, tank car or wrench. For equal stored energies, sparks are the most efficient static discharges in terms of incendivity.

Figure 8 : Spark MIE of Gases Decreases as Capacitance and Electrode Diameter Are Decreased (Example Hydrogen in Air)

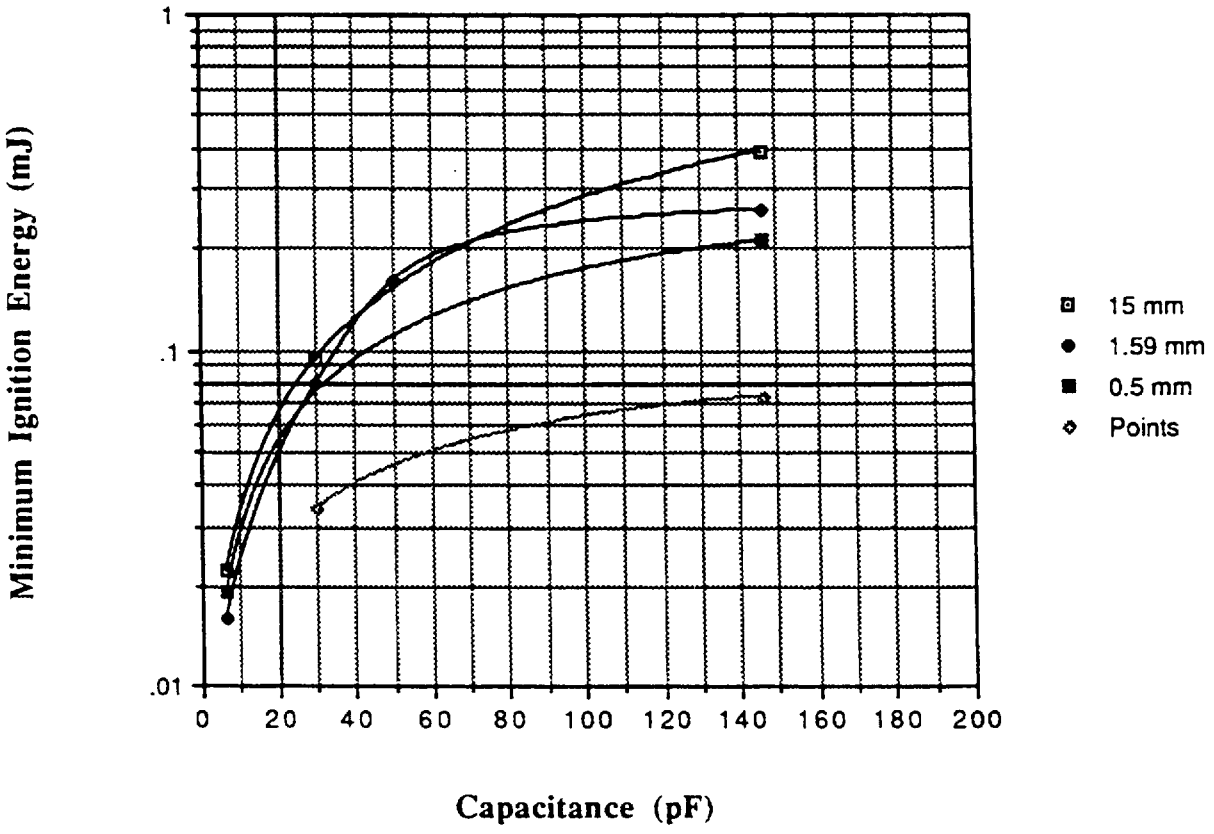
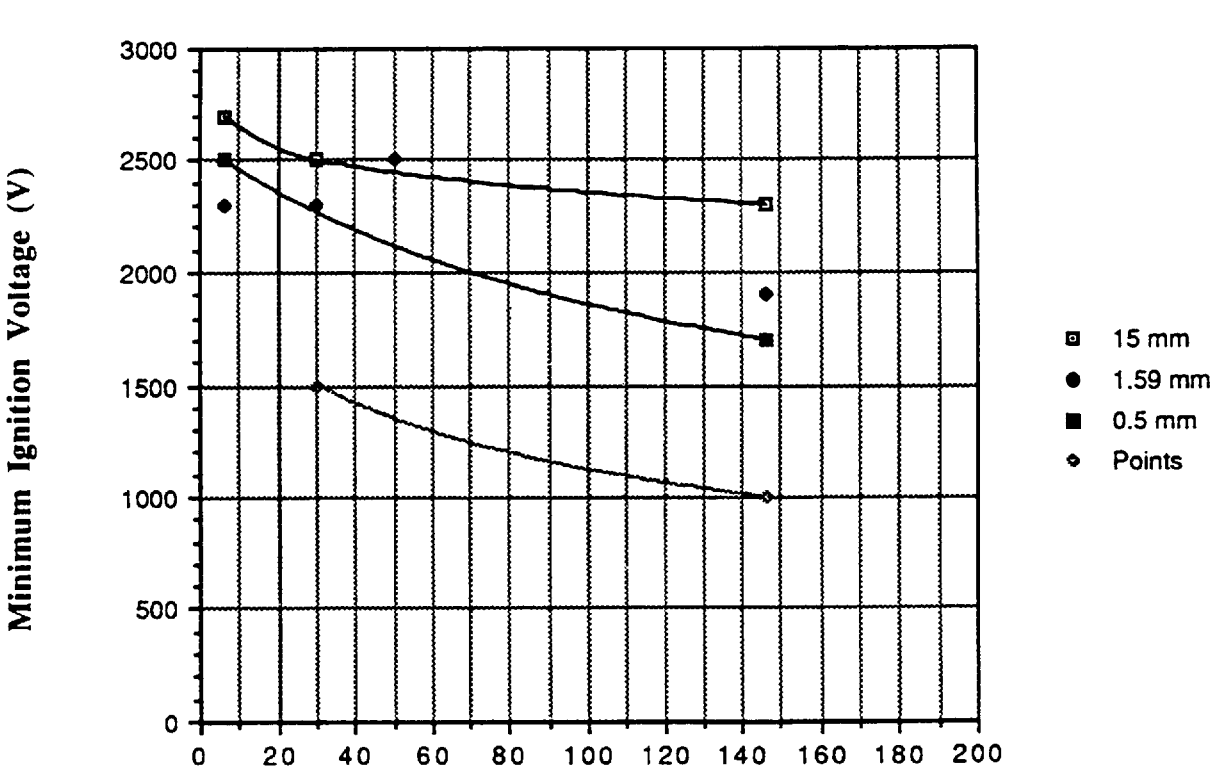


Figure 9 : Minimum Ignition Voltage Decreases with Decreased Electrode Diameter and With Increased Capacitance (Example Hydrogen in Air)



Effect of Capacitance and Electrode Diameter on Minimum Ignition Energy and Voltage

As shown in Appendix C the spark MIE of gases is decreased with decreased storage capacitance and electrode diameter. Figure 8 shows the effect with hydrogen in air. Figure 9 shows that the minimum voltage for ignition is decreased with decreased electrode diameter and also with increased capacitance. In fact, hydrogen in air can be ignited at about 100 V when capacitance is increased to 10000 pF (see "Grounding Criteria"). This information is important when designing tests or when applying data. For example, although hydrogen has a LMIE of 0.016 mJ, most charged components will not have as low a capacitance as 6.1 pF. A person would have a typical capacitance of about 146 pF. Also, pointed discharge electrodes will not usually occur. Hence, LMIE data are conservative in most cases even given an optimized gas mixture.

Capacitance of Objects

The capacitance of objects can sometimes be estimated if the geometry is simple, although this will vary with proximity to other objects which can cause stray capacitance and increase the overall value.

Use of Stored Energy to Estimate Ignition Probability

Corona and Brush Discharges

Propagating Brush Discharge

The propagating brush discharge is the most energetic type of static discharge encountered in process operations and can ignite most flammable materials including powders. Energies of several Joules may be released. The phenomenon is due to the charging of a non-conductive layer (such as plastic) on a conductive substrate (usually metal); the electric field is directed through the dielectric and produces a charged double layer (capacitor). The external electric field is therefore very small and air ionization (allowing discharge of the surface) does not take place. Provided the dielectric resistivity is high enough to allow continued charge accumulation, dielectric breakdown (puncture) to the conductive substrate will eventually occur. If certain criteria are met, the radial surface field surrounding the puncture point will be sufficient to allow flashover via stepped discharge which discharges all the surface within the flashover distance. The stepped discharge process (analogous to lightning stepped leaders) allows flashover at relatively low potentials of a few kilovolts. The phenomenon has been termed "propagating brush discharge" in Europe. It is the stepped discharge process that allows "propagation" of the discharge.

This discharge type can also occur on a charged non-conductor in the absence of a metal backing. If charge accumulation is sufficiently high on one side, the other side can develop a countercharge either via ionization processes or by conduction if this side is semiconductive. The former may occur due to corona discharge from any grounded metal point in the vicinity while the latter can be due to moisture or other contamination that raises the surface conductivity.

Thus, the discharge may develop on an isolated plastic pipe accumulating charge internally by powder flow or by being placed downstream of a liquid microfilter. The outer surface will accumulate a countercharge and under the right conditions the pipe wall may puncture and give massive discharge. If the countercharge is not present, large fields can develop around such pipe and personnel may encounter mild to unpleasant shocks. Also, the small discharges responsible in building up the countercharge via ionization may be ignition hazards. If a propagating brush discharge occurs the energy released (tens of Joules) represents a severe to dangerous shock hazard in addition to ignition hazards both inside and around the pipe. 10 J is a recognized lethal threshold dependant on conditions (resistance to ground, body path etc) involved.

"Effective Energy" Concept

The "ignition energy" of various materials is generally measured using a spark discharge from a capacitor. The stored energy ($W = 0.5\ C\ V^2$) is easy to calculate from the capacitance (C) and voltage across the capacitor prior to discharge (V). The spark approximates to a point source of ignition, since the energy is dissipated rapidly in a small cylindrical volume. It is extremely difficult to measure the energy of spatially extensive discharges such as brushes. Even were this done, the total energy is a poor measure of igniting power relative to sparks. Brush discharge energy is dissipated non-uniformly in a divergent electric field, with a hot spot at the metal electrode end. Much of the energy is dissipated wastefully (with respect to ignition) in the "brush" end of the discharge, so brushes are always less efficient than sparks of equal energy.

To circumvent this difficulty, the concept of "effective energy" has been used to assess either maximum energy or ignition probability for non-spark discharges of various types. Briefly, a gas mixture is made up which has known ignition energy as determined by spark. Then, the mixture is exposed to a series of non-spark discharges. From a count of the relative frequency of discharges producing ignition, ignition probabilities can be established against variables such as

area of dielectric surface, metal electrode curvature, polarity and gap. From these, it is possible to establish ignition probabilities for a variety of cases and then to establish safety criteria.

Acceptability Criteria

There is a probability involved in determining whether static accumulation will cause ignition of a flammable atmosphere. This is true even of spark ignition where the stored energy and geometry can be kept practically constant. In the case of complex discharges such as brushes, there is a wide range of possible power densities. Using the effective energy approach, one can determine ignition probabilities experimentally for particular cases where metal-metal sparks are not involved and the energy cannot be calculated. Examples are plastic tubes or bottles that may be rubbed and give rise to brush discharges, brush discharges from oil surfaces, and discharges from charged people. Gibson [3] discusses the case of charged plastic and argues that "worst case" laboratory conditions of gas composition and humidity (etc) allow a safety criterion to be drawn at a probability of 0.001 rather than 0.0001 as used for rigid risk quantification. Tests made at ignition probabilities of 0.01 and greater may be extrapolated to the 0.001P level. This approach was made for determining the maximum acceptable surface area of charged polyethylene sheet in the presence of gas mixtures of different spark ignition energies. To ensure that the ignition probability did not exceed 0.001 (1 in 1000) the areas could not exceed 10 cm^2 for 0.2 mJ (typical hydrocarbon) and 4 cm^2 for 0.04 mJ (coal gas). A similar approach was taken for polyethylene tubes, which showed that tubes having diameters more than 0.8 cm readily ignited mixtures with ignition energy of 0.2 mJ but a 0.5 cm diameter was intrinsically safe at 0.001P for gas mixtures of ignition energy up to 0.17 mJ. These experiments clearly showed the hazards of even small areas of charged plastic in flammable atmospheres.

STRAY CURRENT ARCS

Radio-Frequency

Until the mid 1970s little work was done outside of military studies in relation to weapons systems. Excell (79) gave a technical and historical background showing that close to high power radio or radar transmitters there is a real possibility that sparks can be produced at discontinuities in metal structures. In these cases the metal structures act as adventitious antennas. Examples include metal cranes (spark gap from hook to load) and bonded fuelling hoses which might constitute loop antennas during make / break contact. Richards and Rosenfeld of Shell [78] gave a more recent review of the problem in relation to gas ignition, electro-explosive devices, personnel burns and computer / process control systems.

Historical examples include [78] personnel injuries (burns) in Honolulu Container Terminal and measurement of up to 1 kV relative to the ground on large jib cranes in Hamburg docks, this latter case being due to a 300 kW broadcast transmitter some 7 km away. An undocumented incident referred to in [78] involved a road tanker explosion at a US gas station caused by a radio transmission from a police officer reporting in.

The effectiveness of an antenna depends on its size and shape plus the radio frequency. Below 30 MHz loop structures such as cranes, tanker loading loops and loops formed by columns and pipes are most effective. In [78] it is shown how to calculate the inner perimeter "P" for typical loop antennas. The efficiency of such antennas varies with the ratio of perimeter to wavelength.

Curiously, rusty surfaces increase the incendivity of sparks created in this way, and the normal ignition criterion for clean metal surfaces of a minimum voltage drop of about 300 V does not apply. The power thresholds for ignition vary with the impedance of the structure. To assess the hazard RF field strength analysis is recommended in conjunction with worst-case antenna assumptions [78]. Comparison is then made with a nomograph showing field thresholds at different frequencies for different gas ignition sensitivities (methane or hydrogen) and antenna inner perimeters. Vulnerable distances of 20 km or more might apply especially for vertically polarized 1-2 MHz signals, assuming an output power of 150 kW feeding an antenna with gain of 7. Remedial actions short of relocation include RF screens, reduction of transmitter power or structural redesign.

An assessment of typical offshore platform hazards in relation to electro-explosive devices [78] indicated that MF and HF radios may present a hazard, individual VHF radios may present a hazard only if several are operating on similar frequencies, UHF (450 MHz) radios present no hazard and nor do line-of-sight or tropospheric scatter installations. Further information relating to onshore use of electric blasting caps is given in [75]. It has been suggested [78] that handportable radios be banned from computer suites and control rooms, since external protection is totally defeated by their close proximity to the systems.

Overhead High Voltage Transmission Lines

Objects close to ground level with overhead UHV transmission lines are situated in an electric field which may be of the order 5 kV/m. Isolated objects or people might give rise to sparks when shorted out. The maximum energy released can be effectively related for an alternating field by the object's capacitance to ground and its open circuit voltage. A practical analysis of short-circuit current was made using an object's individual Norton equivalent network characteristics [77]. Examples were given of a well insulated fence (dry fence posts) and an automobile. Practical measurements supported the analytical method used. While the analysis

used was directed at personnel shock thresholds, the same principles could be used for gas ignition hazards.

Galvanic and Cathodic Protection

Electrical potentials may exist between vessels and mooring structures due partucularly to electrical or chemical cathodic protection. Significant currents can be generated when contact is made electrically and this might represent an ignition hazard. Jet Propulsion Labs [76] made a literature review and practical study of this problem for the US Coast Guard in relation to tanker / terminal operations. It was shown that significant stray currents could be produced when opening the loading circuit, in one case even with two bonding cables and a connected loading arm present. In April 1982 the Coast Guard terminated the project for lack of funds (Federal Register 47, No.73, 16242). To avoid sparking or arcing in loading circuits, insulating flanges (Willcox and others) are commercially available to prevent short-circuits. Insulating hoses are hazardous in this application due to possible discharges from charged non-conductive liquid flow or external tribocharging. Ideally the flange should be semi-conductive to avoid external discharges due to rubbing, but it is highly improbable that a non-conductive flange would represent any significant hazard.

HANDLING RECOMMENDATIONS

(1) UNLINED METAL CONTAINERS

All metal containers for flammable liquids should normally be bonded and grounded so that their resistance to ground is less than 10 Ω. In practice, up to 1 MΩ resistance will drain static perfectly adequately, but such a high resistance would normally mean there is a loose or corroded connection that could suddenly fail altogether. The ground reference should be a water pipe or other metallic point suitable for normal electrical grounding. Normally the ground connection should be an uninsulated braided copper type so that breaks are immediately obvious. In corrosive environments insulated cable might need to be used, in which case routine resistance checks should be made. In critical applications where connections are frequently made and broken, such as drum filling, a ground indicator (such as Crouse-Hinds EGL or Russellstoll GSU) or other warning device might be considered. Such devices might introduce a ground resistance up to about 1 kΩ, but this is perfectly acceptable. Proper grounding clamps (screw types with hardened points) should be used, their size and type depending on the application.

Metal containers should be grounded even when filling liquids at well below their flash-points, whenever there is the chance that a flammable atmosphere might be present. For example, in a drum filling operation involving several different liquids in one area, a flammable atmosphere might result from a previous or adjacent operation. High flash-point liquids such as mineral oils or home-heat kerosene can accumulate static and generate sparks from ungrounded containers.

Stirred Slurries

As shown by Vos et al. [82] hazardous charge densities may be produced in stirred slurries involving either organic or inorganic solid phases. For example, a flash fire was caused by stirring an epoxy resin into xylene of conductivity 50 pS/m. To limit the charge density to safe levels of around 10 $\mu C/m^3$, it was necessary to increase the conductivity to about 1000 pS/m. This could be effected using of the order 10 vol% of polar solvent or small amounts or antistatic additive. BS 5958 cites [82] in suggesting a minimum conductivity of 1000 pS/m or a combination of elevated conductivity and reduced power input from the stirrer. The phenomenon is complex, depending on power input, particle size, conductivity, particle loading and the installation plus materials concerned. For non-inerted operations investigation using a field meter might be justified if the conductivity cannot be increased above 1000 pS/m.

Small Metal Containers

Some authorities [58] allow the omission of grounding of small containers below a certain volume, depending on the static hazard of the liquid loaded. The demarcation volumes are based on the container capacitances and the largest stored energies given reasonable assumptions about the maximum charge density in the loaded liquid. Also, it is tacitly accepted that the volume of the container determines to some extent the risk of the operation by limiting the volume of flammable liquid involved. Table 4 given in [58, p. 8] has some inconsistencies, but basically states that for containers up to 5 liters grounding is not required except for carbon disulfide, which is a non-conductive liquid of exceptionally small LMIE. It neglects other liquids of exceptionally low LMIE such as trichlorosilane. Containers for alcohol (methanol and ethanol) do not need grounding up to 10 liters. It is significant that methanol should be singled out, because although it is conductive it has a relatively low LMIE. The exceptions for alcohols might possibly be based on experimental test results, although [58] does not give any explanations for its recommendations.

Aerosol Cans

Concerns have been expressed about the use of aerosol cans in flammable atmospheres and the possible ignition source that would exist from an ungrounded can, particularly if the can were dropped and punctured. The flammable atmosphere might result from the propellant used. A study [71] found that liquid products developed only 100 volts or less on the isolated cans when suddenly punctured while if the can contained a powder it could charge up to 24 kV with a charge of 5×10^{-6} C, corresponding to a stored energy of 60 mJ on the can. Gas ignitions were obtained only with mixes of powder plus propellant or powder plus liquid plus propellant. It was found possible to use water or other antistatic agent in the formulation to deal with the problem.

Unlined Rail Cars and Tank Trucks

For conductive liquids no special precautions apart from standard bonding and grounding are required. It should be determined that the tank cannot become lined by non-conductive polymer or cooled/crystallized solids. Were thick layers to form, large potentials might build up in the liquid during splash filling, including partial insertion of the drop tube or hose.

For liquids of nominal conductivity below 150 pS/m, which under field conditions (low temperature) might have a conductivity below 50 pS/m, microfilters should be placed 30 seconds residence time upstream. Where a close-coupled filter is required in semiconductive liquid service, such as on a filling lance, it should be determined that at least three relaxation times contacting grounded metal are available between filter and tank. This precludes the location of a filter at the bottom end of a filling tube or hose. If non-conductive liquids are loaded and it cannot be assured that the conductivity will never be less than 2 pS/m the microfilter should be placed 100 seconds upstream.

The maximum flow velocity-diameter product for non-conductive liquids top filled through smooth bore pipes and hoses should not exceed 0.50 m^2/s and in no case should the flow velocity exceed 7 m/s. Smooth bore pipes and hoses should be used in preference to hoses containing an inner spiral or equivalent turbulence generator (rough bore), which can greatly increase charging. For bottom filling the velocity-diameter product should not exceed 0.36 m^2/s. Operation at lower product values is desirable.

Splash filling of non-conductive liquids should be avoided even for liquids of high flash point since they may generate a flammable mist.

Slow start filling is beneficial for avoiding discharges to the filling pipe (or hose) and in reducing mist formation in combustible liquid service. It is required when the product contains more than 0.1% free water and should limit the flow velocity to 1 m/s until the fill pipe is submerged.

These procedures are required for flammables (including cases where switch loading might occur) and for combustibles loaded in such a way that significant amounts of flammable mist (or foam, a mist precursor) may form.

Floating Roof Tanks

Two types of floating roof tanks are conventional "open-top" tanks and "hard hat" tanks. The latter have external weather roofs over the floating roofs which, together with the shell, form a Faraday Cage over the floating roof. The hard hat tanks therefore should offer additional protection against ignition by lightning and by personnel [81]. However, questions have been raised about whether vapors might be trapped between the floating roof and the weather roof.

Tests with gasoline [81] showed that this might occur particularly during filling of an empty tank and prior to floating of the roof, but that once the roof is floating the vapor concentration diminishes rapidly to a negligible level. The bond between the floating roof and shell must be entirely dependable and the need for inspection must be incorporated in the design. Personnel should not be permitted on the floating roof except for inspection and maintenance following adequate preparation and supervision. When receiving into an empty tank, hand line gauges or samples should not be taken for 12-18 hours (depending on wind conditions) after the roof has begun to float [81].

For floating roof tanks in general, liquids with conductivities less than 50 pS/m should be treated as static accumulators until the floating roof is buoyant. This may involve upstream filter placement, velocity and splash-fill restrictions plus precautions in the presence of a second phase such as water (slow start). The restrictions recommended in BS 5958 are similar to those for road tankers.

Unlined Drums

Drums are often grounded by resting on grounded weigh scales, but in general it must be verified that grounding exists. This is because drums can accumulate thick paint coatings or other non-conductive layers which can defeat "contact" grounding. Clamps such as the Crouse-Hinds 20109B assembly or its equivalent are designed to penetrate to the underlying metal.

Drums should preferably be bottom filled using a lance with pointed tip. This is strictly necessary only when non-conductive liquids are handled, plus a high amount of charging occurs (such as from a microfilter). The pointed lance tip (for example, a 45 degree cut-off at the tip) discourages incendive brush discharge formation and instead promotes non-incendive corona. If only conductive liquids are being drummed, splash filling is allowable.

To avoid the dripping from the extracted lance after filling, equipment is available to maintain the lance above the liquid surface while ensuring that a corona discharge device stays in the liquid.

Drum Pumps

Drum pumps should be equipped with syphon breakers.

(2) INTERNALLY COATED METAL CONTAINERS

A metal container with an internal coating of paint or epoxy/phenolic resin up to 20 mil (0.5 mm) thickness can be treated as unlined. Often such coatings are less than 10 mil thick. Thin coatings have a large capacitance and charge trapped at the boundary does not contribute significantly to electric field in the vapor space. Also, such coatings usually have resistivities several orders of magnitude less than thermoplastics such as polyethylene. There is no evidence that propagating brush discharge can occur in this situation.

Thicker coatings and larger volumes may give rise to a hazard if conductive or semiconductive liquids are sprayed in, creating large charge densities. If devices such as deflector/thrust neutralizers are used in a road/rail tanker, large charge densities might be created by the high velocity lateral jets. For conductive and semiconductive liquids, only a few kV surface potential is needed to give an incendive spark. The surface potential is readily estimated by treating the area of the contacted walls as a plane capacitor, where the charge is given by the total charge loaded to the tank. Where a coating must be used with devices that can create large charge densities, and bottom filling is not used, a discharge electrode of a compatible metal might be considered. This might consist of a vertical grounded rod or metal grid attached to the tank floor.

(3) PLASTIC LINED CONTAINERS

Plastic linings such as polyethylene are typically more than 20 mil thick and have very high resistivities that electrically isolate the liquid from the container shell. The shell must be bonded and grounded as with unlined metal containers. Special precautions are needed for both conductive and non-conductive liquids.

Splash filling should not be done and instead, bottom filling using a lance with a pointed tip is required. The hazard of splash filling may be greater for conductive and semiconductive liquids than for non-conductive liquids. This is because the more conductive liquids can release more energy in a single discharge. Conductive liquids may release much of their total charge in the form of a spark to the filling pipe, and ignition may occur for liquid potentials of only a few kilovolts (as opposed to more than 20 kV for incendive brush discharge from non-conductive liquids).

Plastic Lined Fiberdrums

NFPA 30 recently voted negatively on Tentative Interim Amendment #334 proposing to permit storage of flammable liquids (Class 1B and 1C) in fiberdrums. Major concerns were with fire exposure, weathering and breakage during dropping (for example the 4 ft drop test). Future use of these will likely be limited to Class II and III combustible liquids as in the case of polyethylene drums.

(4) ALL-PLASTIC, GLASS AND COATED GLASS CONTAINERS

All-plastic containers cannot be grounded unless they are constructed of a conductive or semiconductive plastic. Any isolated metal of patches of water on the surface may be sources of sparks. Non-conductive all-plastic containers in excess of 5 liters should not generally be used for "flammable" liquids. Where their use is required (such as disposable sample bottles) the smallest size needed to do the job should be selected. Where the flash-point of the liquid is high relative to handling temperature, such as FP > 90°F, a variance might be made in some cases where the use of plastic is essential. For example, pentanedione and certain other fine chemicals cannot be stored in steel drums and lined drums (including polysteel) have given problems. In such cases plastic might be used provided adequate handling procedures are employed and full compliance is made with OSHA and NFPA 30 restrictions regarding storage. It is essential not to store plastic drums in the vicinity of flammable atmospheres owing to possible brush discharges from their surfaces during handling. The drum should not be opened if the ambient temperature is close to the flash-point of the stored liquid, such as within 10 °F of the flash-point. The margin of safety adopted should anticipate the possibility of elevated liquid temperature if the storage temperature has not been carefully regulated. The liquid may retain an elevated temperature for an extended period after transport or storage at high ambient temperature (truck, sunlight, storage shed). This problem would of course exist were the flash-point slightly above 100°F (combustible) rather than slightly below 100°F (flammable), since the demarcation for "flammable" is arbitrary.

Non-conductive (particularly plastic) containers give rise to hazards by charge accumulation and by induction:

(i) Charge Accumulation

Since plastic containers such as polyethylene are extremely good insulators, charge flowing in will accumulate independent of the conductivity of the liquid. The quantity of charge will depend on the volume of the container and the charge density in the liquid stream. Accumulation and static discharge from the liquid can be mitigated by bottom filling using a

grounded metal lance with pointed tip. However, this does not prevent charging of the outside container wall, and the possibility of incendive brush discharges must be considered.

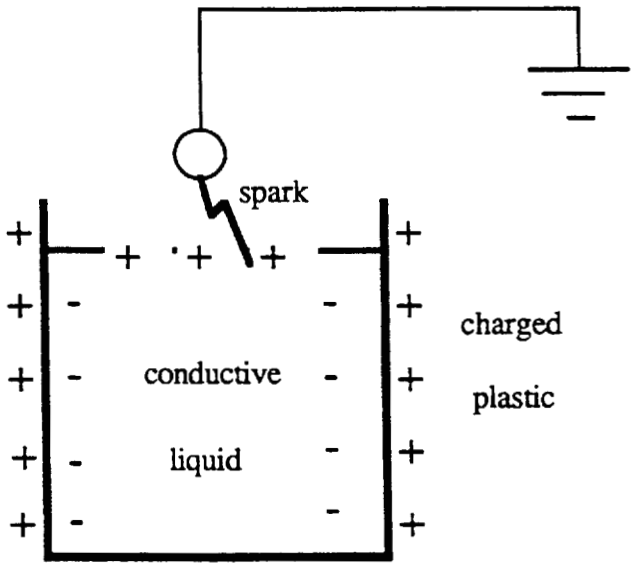
(ii) Induction

Figure 10 shows the principle of charge induction from an externally charged non-conductive container such as a plastic beaker or bottle. External charging is most likely to occur in dry weather (relative humidity < 45%) and may be caused by removal of the container from a bucket stack, from a coat pocket (etc) or by surface cleaning. The external charge attracts opposite charge from the liquid to form an internal charged layer. In the case of a conductive liquid especially, this layer is tightly bound by attraction to the non-conductive wall leaving a net countercharge in the body and on the surface of the liquid. The simple act of rubbing the outside of the container can elevate the liquid potential to thousands of volts, and sparks may be produced at the surface to any of the following:

- o metal filling pipe
- o finger
- o sample thief
- o conductive stream of liquid flowing in

Conductive liquids are especially prone to this phenomenon and there have been numerous incidents of fires with methanol and isopropanol (methanol furthermore has an unusually low ignition energy and forms its most easily ignitable mixture in air at 25 °C).

Figure 10 : Charge Induction from Plastic Container on Conductive Liquid Surface



The third example given above (discharge to stream of liquid flowing in) is particularly interesting and has been theorized as the only explanation for one incident. While a stream of conductive liquid can form a path to ground, this is only the case up to the break-up length for the jet. Otherwise, it is a discontinuous stream. As a charged container is being filled, the liquid jet from the filling pipe decreases in length and finally constitutes a continuous stream to the surface. Shortly before this occurs, there will exist a spark gap between the surface and the stream. If the

correct mixture is present and the system has sufficient potential and capacitance, a spark may ignite the vapor.

Non-conductive liquids are unable to discharge a significant portion of their charge in the form of a spark and are less prone to induction. Thus, they are safer from the standpoint of this hazard.

Glass bottles are safer than plastic in terms of static discharge, but have the disadvantages of breakage and difficulty in disposal (plastic sample bottles can readily be incinerated). The breakage problem of glass bottles can be mitigated by selection of types having chemically-resistant thermoplastic coatings designed to prevent shattering and to provide containment of the liquid (Wheaton Safety Container Co). No static hazard evaluation of the coated glass bottle is available.

(5) HOSES

Hoses are available in several types which can be broadly grouped into:

(1) "Conductive" : a hose with an incorporated grounding element (usually spiral or braid) between the end connectors but whose carcass can be totally non-conductive (polypropylene etc).

(2) "Semiconductive" : a hose made from a static-dissipating material such as carbon-impregnated rubber. The static dissipating material is often applied as the outer hose layer. The hose may contain metal spirals or braids to give strength, but these are not in electrical contact with the end connectors. This is because this type of hose is frequently used for aircraft fueling, and in case of ground faults the semiconductive hose has too high a resistance to allow the passage of large ground currents which could melt the hose or ignite the fuel.

(3) Conductive hoses featuring both grounding element and semiconductive carcass or liner.

(4) Conductive stainless steel flexible hoses (various types).

(5) "Non-conductive" : a hose made entirely of non-conductive material

All of these hoses except (5) provide "static" bonding between the equipment at both ends. The conductive hose does this via the grounding element provided that this is in good condition (continuous and bonded to the end connectors). Unless equipped with a grounding element the semiconductive hose does not provide low resistance (< 10 Ω) bonding. To dissipate static, the resistance from any point of the hose to the connected equipment should be less than 10^8 Ω. Independent grounding of the equipment should be considered where resistance is above 10^6 Ω. One advantage of semiconductive hoses is their relatively high resistance (10^5-10^8 Ω) which prevents the passage of large currents in the event of power equipment failure. Several fires have occurred during aircraft fuelling owing to large currents passing through the grounding wires of "conductive" hoses, which then acted as electric heater elements. A disadvantage is that semiconductive hoses can become exceptionally stiff and brittle in very cold weather.

Hose types 1-4 also provide protection against static accumulation and discharge inside the hose where non-conductive liquids are handled. Types (2) and (3) are superior in this area since their inner surfaces are semiconductors and rapidly dissipate static. Types (1) and (4) may be subject to internal discharges if the inner sleeve is non-conductive. This may lead to "pin-hole" punctures to buried metal spirals. Whether incendive discharges can occur from non-conductive

inner sleeves during hose draining is not known, but since the electric field is mainly directed radially outwards this should be hazardous only in extreme cases such as if drainage from a microfilter occurred. This might cause sufficient static accumulation on the internal hose surfaces for lateral discharge to occur. For this reason, hoses downstream of microfilters in non-conductive liquid service should have static-dissipating properties such as antistatic liners or uncoated metal inner components. All-metal pipe is preferred.

Non-conductive hose should not be used in flammable liquid service or in a flammable atmospheres. This is because surface rubbing might create incendive discharges. Also, in non-conductive liquid service, such hoses can accumulate enough internal static to give a propagating brush discharge, often involving puncturing of the wall. This should only occur downstream of a significant static generator such as a filter.

When loading open dome tank cars and trucks with flammable liquids, hoses of types (3) and (4) are recommended. An accident was believed caused when reinforcing wires in a neoprene loading hose were isolated from ground and exposed through the carcass. The spark was believed to have occurred from the isolated metal wires to the dome.

When overhead loading a non-conductive liquid into a tank car or truck via a flexible hose connection using a stainless steel flexible hose, some time should be allowed after filling before removal of the hose. As the hose is removed (or if the hose falls back into the liquid) there is the chance of liquid surface discharge to the end. As in the case of sampling and gauging, about 3-5 minutes should be allowed for charge relaxation. If a two-phase mixture (for example water plus oil) has been loaded, at least 30 minutes should be allowed so that the settling potential has time to dissipate.

Periodic testing of electrical continuity of hose ground wires is required.

Hose Disconnection

It is essential that when disconnecting hoses from trucks (and other containers) after unloading, the tank valves are first shut. Failure to do this was a contributory event in a recent toluene tank truck explosion and fire that seriously burned two people. Valve closure prevents any external ignition source from allowing flash-back into the tank. Since any explosion will occur in the vapor space, an "empty" tank containing vapor-air mixture is the worst-case.

(6) PERSONNEL

6.1 *Personnel grounding is required in NFPA 77 and BS 5958 where people come into contact with flammable atmospheres. BS 5958 introduces this need whenever the atmosphere has a MIE of less than 100 mJ.*

Origin of BS 5958 "100 mJ" Criterion for Personnel Grounding

People involved in industrial operations have attained body potentials of 10-50 kV due to static charging, corresponding to stored capacitor energies in the range 5-375 mJ (assuming a range of body capacitances from 100-300 pF). Studies cited by Gibson [12] have shown that for gas ignition, the effective energy of a discharge from the human body is only about one-quarter that of a spark of equal energy. Other studies with dusts gave similar ratios of between one-half and one-third efficiency relative to sparks of equal energy. As a result BS 5958 set a 100 mJ criterion for the maximum ignition energy of a flammable mixture (as determined by spark) that should be at risk of ignition by a charged person. The criterion is conservative in view of the very

high maximum body potential considered; owing to the V^2 dependence of energy the usual range of stored body energies is far smaller.

6.2 *Grounding via the floor should give a body resistance to ground less than 100 MΩ, and can be achieved using conductive/antistatic shoes or a foot grounder, plus a conductive floor in the flammable work area. The latter may be effected using a grounded plate/grid or with the use of conductive paint. The floor must be kept free of insulating deposits. An alternative to grounding via the floor is to use a grounding bracelet.*

Conductive shoes

Conductive shoes or boots give a body resistance less than 500 kΩ to ground and meet the criteria given in NFPA 99, MIL B-81705B, EIA-1S-5A or ASTM D-257-78. BS 5958 defines conductive footwear as having a resistance less than 150 kΩ, or in practice giving a body resistance to ground less than 100 kΩ. Typical resistances of commercially available shoes are a few thousand ohms. Safety shoes and boots are commercially available.

Antistatic Shoes

Antistatic shoes or boots via BS 5958 Part 1 (1980) have a resistance between 50 kΩ and 50 MΩ, but in practice should give a body resistance to ground between 50 kΩ and 100 MΩ. NFPA 99 defines "antistatic" in terms of the decay time measured by one of two standard methods (4046 of Federal Test Method Standard 101B or 76-1972 of ANSI L14.112). Typical resistances of commercially available shoes such as Lehigh "Positrax" safety shoes are of the order 10 MΩ.

Foot Grounders

A variety of foot grounders are available. They consist essentially of a conductive neoprene rubber attachment on the sole or heel of the ordinary shoe/boot which connects to the bare skin of the lower leg using a wire connection to a conductive garter strap. An alternative type uses a conductive innersole inside the shoe. The devices can be purchased using a range of available resistors built in to give the desired body resistance to ground.

Wrist Straps (Grounding Bracelets)

These consist of a snug strap around the wrist plus a grounding cord that connects to any available ground terminal. They are available in a variety of resistances and styles, such as straight cord, coiled cord, alligator/bulldog clip termination, etc. The resistance to ground is determined by the size of resistor incorporated into the snap end (typically 1 MΩ), which is a safety feature designed to prevent electrocution when working near powered systems. They typically use banana plug inserts in the clip to allow fast decoupling. The devices may have application for fume hoods or can be hung from overhead to give some mobility while avoiding trip/tangle hazards.

Conductive Floor

Per NFPA 99 the conductive floor shall have a resistance between 25 kΩ and 1 MΩ using prescribed test methods. No deliberate ground connection to the floor is required. For chemical industry (not health care facility) application the lower resistance limit is unnecessary and the conductive floor can be grounded metal such as steel grid walkway. For grounding of personnel

in most chemical industry applications, provided the body resistance to ground is less than 100 MΩ everywhere on the floor the fundamental grounding need has been met.

Specification Test Devices

Simple testers are available for checking the resistance of grounding bracelets while being worn. The Legge model #WT25 accepts and passes resistances in the range 0.75 - 10 MΩ. A "stand-on" device is also available (model SLTM-1) for checking conductive footwear. It reads "green" in the range 0 - 2.25 MΩ, however, and is therefore not ideal to measure resistances in the usual range for antistatic shoes (typically about 10 MΩ). The instrument could be modified using shunts according to the type of shoe to be used. BS 5958 Part 1 (1980) gives the electrical circuit for a device to check antistatic shoes (up to 100 MΩ). Legge also supplies a floor conductivity tester (model #LA-1) to ensure compliance with NFPA 99. It reads in the range 10 kΩ to 5 MΩ.

Suppliers

Special items are available from Walter G. Legge Company Inc., Static Control Division, 444 Central Avenue, P.O. Box 591, Peekskill, NY 10566. Toll Free 1-800-345-3443. Antistatic safety shoes are available from Lehigh Safety Shoe Company.

Practical Problems with Personnel Grounders

Where personnel might walk in areas containing powders or lacquer-type solutions capable of rendering the floor or shoe contact non-conductive, the need for frequent (daily) inspection and testing is an important consideration. It is recommended by suppliers that special test devices be purchased for regularly checking effectiveness of floor and footwear grounding.

It is recommended in BS 5958 that antistatic or conductive gloves be worn when handling metal objects (wrenches etc) in flammable atmospheres so as to avoid sparks from the ungrounded object. That is, no type of personnel grounding will avail if the person is wearing non-conductive gloves. However, unless some mechanism exists to attain high potentials on the metal object, such as proximity to a charged plastic surface, this provision might be seen as too conservative. Where non-conductive gloves must be worn owing to industrial hygiene considerations it is hardly practical to ground the metal item unless it is in common use at the location and can be permanently attached to a grounding cable.

While it is impractical to issue special shoes to people temporarily in a designated hazardous area (since one would need to maintain a store of sizes and preferably sterilize them before reissue) the foot grounder can be checked out in the same manner as goggles and helmets. Even foot grounders have a logistics problem in that personnel wearing a variety of shoes or boots will have different needs; for example, a foot grounder designed for a flat shoe will not work with a boot. Rather than stock a variety of foot grounders, the Legge "Heelstat" might be considered as it works for both flat and heeled shoes. The grounding bracelet is unaffected by this problem or by floor contamination but is often an encumbrance owing to its grounding cord. Also, as in the case of foot grounders, the body connections of bracelets are subject to loss of effectiveness over time so these must also be regularly tested.

A final problem is how to designate the area in which the devices should be worn and in which the floors should be conductive. An entire building containing a drum filling operation might be electrically classified while it is evident that the static hazard due to personnel only exists

in the immediate vicinity of opened drums. This follows from the consideration that were the general area considered to be susceptible to vapor ignition by static discharges from people the vapor concentration would be toxic in almost every case and well above the STEL in most cases. If the entire building were designated for personnel grounding, every visitor, supervisor and inspector would need to be issued grounding devices and the entire floor area would need to be conductive for the policy to make any sense. The best solution is to literally interpret the electrically classified area (NFPA 30) and supply a grounded metal floor covering (grid or plate) only in this area, for example, the immediate vicinity of the container involved. To address the visitor problem, designated walkways can be painted on the floor outside the area considered a flammable vapor hazard.

Origin of "<100 MΩ" Criterion for Static Grounding of People

Justification for this was described in [6] using two approaches.

In the first it was assumed that the person receives a continuous charging current and acts as a leaky capacitor. From Ohm's Law even were the charging current as high as 10 μA, a ground resistance of 100 MΩ would maintain a body potential of only 1 kV. For body capacitances in the range 100-300 pF the stored energy at 1 kV is in the range 0.05 - 0.15 mJ, below that of most flammable vapor-air mixtures even neglecting the efficiency factor of one-half to one-third [12] for discharges from people.

In the second the time taken for a leaky capacitor to discharge having received a single initial charge was considered. From equation A.6 the charge will relax by a factor e^{-1} (37% of its initial value) in one time constant and almost completely disappear (0.67% of initial value) in five time constants. Since the time constant is the product of resistance and capacitance (RC), and a range of body capacitances from 100-300 pF, the range of time constants at 100 MΩ is 0.01 - 0.03 seconds.

Early work addressing the area of operating theaters [69] concluded that a specification for antistatic rubber should involve a resistance between 100 kΩ and 10 MΩ. It is evident that this area represents an extreme case since gases with low ignition energy enhanced by oxygen-enriched atmospheres are present both in equipment and the patient's lungs.

6.3 *To prevent electrocution risk should the person contact a power source, the resistance of the shoe or other device should be more than 100 kΩ.*

Origin of "> 100 kΩ" Criterion for Static Grounding of People

Justification for this was described in [6] using Ohm's Law. The threshold "can't let go" response to AC current is 6 mA. For a body resistance of 10^5 Ω, this current will not be exceeded at up to 600 volts AC. For lower supply voltages, the response will vary from imperceptible through perceptible to annoyance, depending on the individual [50]. DC response threshold currents are considerably higher. Hence, the minimum ground path resistance should avoid hazardous shock from powered equipment due to the grounding device. It will not, of course, prevent shock if a ground path is completed by any other part of the body.

Hazards of Clothing

6.4

Personnel Grounding and Clothing for Highly Sensitive Atmospheres

Where flammable mixtures of very low ignition energy are present, such as in operating theaters or when handling explosive dust, typical precautions in addition to footwear and floor conductivity (see above) include the use of antistatic clothing and (particularly in the explosives industry) the prohibition of jewelery including rings and wrist-watches that might be spark sources. In the latter case, this also lessens the risk of sudden mechanical impact by a hard surface.

(7) SAMPLING AND GAUGING

After loading, charge in the bulk of the liquid relaxes to the walls and free surface, and the potential at the free surface can continue to rise for some time after loading. If a second phase is present such as free water or solids, either from the loading circuit or from the tank heels, a settling potential can be created as the second phase falls out. Literature and Standard recommendations give various "wait" periods prior to sampling or gauging of non-conductive liquids loaded into tanks and tankers. The "wait" period should depend on the liquid conductivity, the size of the tank and the presence of a second phase.

(8a) METAL PIPELINES

It is found that metal pipelines are almost invariably grounded at several points by virtue of their connection to equipment and other grounded points. It is not usually necessary to use jumpers or special grounding cables. Spot tests on plant pipelines have shown that Teflon or other plastic coatings on nuts and bolts at flange connections do not prevent continuity, but if this is a concern it can be taken care of using star washers. The criterion for static grounding of pipelines and other large equipment is that the resistance to ground should be less than 1 megohm from every point.

Jumpers may be needed on line items such as flow meters that represent interruptions in electrical continuity. The need for jumpers around swivel connections is not acknowledged by all sources but there should be little impediment to taking a conservative approach. A conductive liquid will provide its own continuity with regard to static when the line is full. After drainage and evaporation however, one would require continuity to prevent internal or external sparks due to any mechanism.

Special grounding jumpers are sometimes used on pipelines containing unstable or autodecomposable materials such as peracetic acid and acetylene. However, no evidence for their necessity is available even from the point of view of direct lightning strikes. On oxygen lines, Kirk cells are often installed for lightning protection since resistance heating can sometimes start a fire involving combustion of the inner wall.

(8b) LINED METAL PIPELINES

BS 5958 states that liquids with conductivity up to 1000 pS/m can accumulate hazardous levels of charge on pipelines with high resistivity linings and coatings. An ignition might occur as the pipe drains (see also hoses). Criteria given in BS 5958 for the safe use of linings provide that before the hose can drain, a minimum relaxation time must be allowed. This time must exceed the shorter of (t_1, t_2), where these times are defined by:

o $t_1 = 3 \cdot \rho \cdot \varepsilon_o \varepsilon_r$

	r	=	lining resistivity (Ω.m)
	ε_r	=	dielectric constant of lining

That is, 3 relaxation times for the lining material, or:

o	t_2	=	$(L^2 \cdot \varepsilon_r \cdot \tau_L) / (\varepsilon_L \cdot d \cdot r)$

where	ε_L	=	dielectric constant of liquid		
	τ_L	=	relaxation time of liquid	= $(\varepsilon_o \cdot \varepsilon_L) / \sigma$	(s)
	σ	=	conductivity of liquid (S/m)		
	L	=	distance between grounded points in contact with liquid along the pipe (m)		
	d	=	pipe lining thickness (m)		
	r	=	pipe radius (m)		

Derivations and references for these criteria are not given in BS 5958.

(9) INLAND AND MARINE LOADING AND UNLOADING OPERATIONS

Grounding of vessels is not necessary since they are already grounded by contact with water. To avoid stray currents, bonding is usually not carried out and instead an insulating flange is inserted into the loading line with the lines on each side being continuously bonded. Long lengths of non-conductive hose are less desirable than the flange when non-conductive liquids are being handled and might be hazardous if placed downstream of a filter. In addition to the precautions for tank car and truck loading, special precautions such as ullage space inerting should be considered for non-conductive liquids since safe loading rates have not been clearly established for large tanks. Inert gas systems may in some cases be mandated. BS 5958 recommends use of a 1 m/s slow start until the tank inlet is covered with liquid, and that 1 m/s flow velocity be maintained when a second immiscible phase is present. BS 5958 further states that there is no evidence of flow velocities up to 7 m/s being hazardous. As in the case of tank trucks, plastic pipe should not be used in the filling line.

(10) VACUUM TRUCKS

Available information [10, 11] does not indicate any history of static problems when using vacuum trucks, although this might be due to their normal mode of use rather than any intrinsic safety. Most trucks are made for use in water service such as sewerage, sludge, etc., and might not be suitable for flammable or combustible liquid service. Hoses normally supplied are non-conductive and the vacuum pump usually discharges at grade [10]. While most liquid pick-ups should be highly contaminated with water, dirt, etc., and have a high conductivity, precautions should be taken if flammable or combustible liquids might be picked up, particularly if the liquids might be non-conductive and water-immiscible.

Of 12 vacuum truck fires considered in [10] the tank truck engines were usually the cause of ignition owing to the truck being located too close to the spill pick-up point. One or two cases were probably due to exhaust backfires or sparks, and two cases were possibly caused by vacuum pumps discharging at grade near the engine. Concerns existed that ignitions might be caused by pick-up of rocks (flint-type sparks) and other sparking objects, or whipping of discharge hoses during unloading. One unloading accident might have been caused by an impact or static spark from a coupling one the end of an unloading hose dropped into a storage tank.

In [11] it states that the use of bonding cables and venting above the truck through a safety venturi will eliminate most fires. The following recommendations extracted from [11] are relevant to ignition hazards:

- Power the vacuum drive from the truck engine power take-off rather than a separate engine. Engine exhaust stack to be vertical and not under the truck. No catalytic converter or excessively hot attachment to be present.

- Discharge vapors through safety venturi 20 feet above the truck. Venturi will dilute vapors below lower flammable limit (although vapors may become flammable during last 1-3 minutes of loading). Design should prevent vapors accumulating under or near the truck at grade while loading on vacuum.

- Discharge flammable liquids by gravity flow or regular pump rather than by air pressure (note that air pressure discharge is a general unsafe practice for flammable liquids).

- Each truck should be equippped with a combustible gas detector. Tests should be made on a calm day before pick-up of a flammable liquid, whenever the truck is downwind of the pick-up point.

- Check safety valve routinely and schedule annual check and service of valve.

- Bond truck to source and ground source whenever flammable liquids are loaded or discharged (exception : remote flammable liquid spill).

- A minimum 30-40 feet of hose suggested for loading purposes to keep the truck a safe distance from a flammable liquid spill.

- Position truck upwind of flammable liquid pick-up if possible, otherwise cross-wind, and downwind only if gas detectors show no flammable vapor present. If little or no wind is blowing do not pick up flammable liquids unless gas detectors show no flammable vapor is present. Keep truck at least 30-40 feet away from spill area.

To the above could be added specific precautions when handling relatively pure non-conductive products such as hydrocarbons. These would be similar to those for tank trucks and include the use of conductive or semi-conductive hose, with bonded end-connectors. Several other recommendations in [11], such as chemical compatibility and fire protection should also be considered but are not relevant to static electricity per se.

RECOMMENDATIONS FOR FURTHER WORK

(1) A project is recommended in which an electrically isolated tank truck (or less desirable, a tank of similar dimensions) would be grounded through an electrometer and filled with a high flash point mineral oil with a conductivity of about 2 pS/m, either through a pipe or a composite "rough bore" hose. The measurement of streaming current would determine whether such hoses are a cause of mysterious fires. Simultaneously it would be possible to use an image intensifier to observe any electrostatic discharges in the truck. An unbaffled truck would simplify this. Grounded probes could be used to simulate truck internals. Both top and bottom filling might be carried out using image intensification to verify the BS 5958 recommendation to limit bottom fill flow rates to 25% those of top filling.

(2) Research is recommended to determine whether inner non-conductive sleeves in pipes and hoses are a brush discharge hazard during hose drainage and whether antistatic hose liners (such as used by Willcox) are needed in non-conductive liquid service where spiral breakage is not present.

(3) Plastic manually-operated drum pumps are frequently used to transfer flammable liquids and there has been a report of a fire originating inside a drum being transferred from. It appeared possible in this case that a brush discharge occurred from the pump handle being operated at the time, although a discharge from the operator might alternatively have occurred. The liquid was conductive. No published information has been found on drum pump hazards and some study should be made.

(4) Theoretical and experimental studies of the effects of non-conductive liners and excess charge at free liquid surfaces are needed. While it is unlikely that propagating brush discharges are produced on plastic liners in liquid handling systems, this possibility is considered by various authors.

(5) Filters are being used on lances when handling conductive and semiconductive liquids. Research is needed into whether this practice is safe, particularly when filling lined tanks and drums. There would appear to be a problem during the early stages of filling especially.

(6) In the Petrochemical Industry the use of lances is often limited by personnel exposure problems when handling toxic or malodorous liquids. Research is needed as to whether splash-filling of lined drums is an acceptable procedure and what the limitations (liquid conductivity, liner thickness and resistivity etc) should be. In some cases the exposure problem can be mitigated by the use of a spring-type discharge electrode on the end of the lance, which uncoils into the liquid during flow, minimizing wetting of the lance itself. Such devices are relatively unheard of but may be purchased by special order.

(7) There have been numerous studies of brush discharges from liquid surfaces but apparently none on the formation and effective energy of the "go devil", a surface discharge that can be several feet in length and which is somewhat analogous to the "wall-to-cone" (or "bulking brush") discharges seen during silo filling. By analogy one might expect the effective energy to be greater than for brush discharges, perhaps around 10 mJ. Such discharges might be responsible for mist ignition of high flash-point liquids.

(8) It is recommended that the industry hold discussions with container manufacturers to determine the feasibility of antistatic plastics for use in all-plastic drums and other applications. For example, conductive carbon black-loaded polyethylene may be directly bonded to an inner polyethylene drum shell allowing direct grounding while avoiding the

mechanical problems of polysteel drums and retaining the advantages of a polyethylene liner. The conductive plastic will have a greater thermal conductivity than HDPE and may improve fire resistance by the Factory Mutual test. By improving the fire resistance with respect to steel drums the present restrictions on plastic drum storage might be eased. A groundable plastic drum would present no external discharge hazards and for conductive flammables could be safely loaded and unloaded using a metal dip pipe.

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Glossary of Terms

A	Area	(m^2)
B	Mass transfer number	(dimensionless)
BP	Boiling Point	(°C)
C	Capacitance	(°F)
$c_{p,a}$	specific heat of air at constant pressure	(J / mol-K)
d	Diameter	(m)
$D_{3,2}$	Sauter mean diameter	(μm)
E	Electric field	(V/m)
F	Volume flow rate	($m^3.s.^{-1}$)
g	Acceleration due to gravity	($m.s.^{-2}$)
ΔH	Energy required to vaporize liquid	(J / mol)
I	Current	($C.s^{-1}$ or A)
IBP	Initial Boiling Point	(°C)
I_L	Leakage current	($C.s^{-1}$ or A)
I_s	Streaming current	($C.s^{-1}$ or A)
gpm	Gallons per minute (US)	
igpm	Imperial gallons per minute	
J	Current density	($A.m^{-2}$)
L	Length	(m)
L_v	Heat of vaporization	(J / mol)
LMIE	Lowest Minimum Ignition Energy	(mJ)
LOC	Limiting Oxidant Concentration	(vol% or mol%)
MIE	Minimum Ignition Energy	(mJ)
n	ionic number concentration	(m^{-3})
n_i	number of droplets of diameter d_i	(dimensionless)
q	Ionic charge	(C)
Q	Charge	(C)
dQ	Charge element	(C)
R	Resistance	(Ω)
R_L	Leakage Resistance	(Ω)
s	Surface Charge Density	($C.m^{-2}$)
S	Volume Charge density	($C.m^{-3}$ or $\mu C/m^3$)
S_∞	Steady state charge density in long pipe	($C.m^{-3}$ or $\mu C/m^{-3}$)
t	Time	(s)
$t_{0.5}$	Half-value relaxation time	(s)
T_{bp}	Liquid boiling point	(K)
T_f	Initial fuel temperature	(K)
ΔT_{st}	Temperature rise for stoichiometric combustion	(K)
v	Velocity	(m/s)
V	Volume	(m^3)
VP	Vapor pressure	(kPa or psia)
W	Energy	(J)
α	Conductivity temperature coefficient	(K^{-1})
β	Constant in Schon-type charge density equation	($C.s.m^{-4}$)
γ	Surface tension coefficient	($N.m.^{-4}$)

δ	Charge transferred in discharge	(C)
ε_o	Permittivity of vacuum	($F.m^{-1}$)
ε_r	Dielectric constant	(dimensionless)
ζ	Zeta potential	(V)
η	Viscosity	(kg / m-s)
μ	Ionic mobility	($m.^2V.^{-1}s^{-1}$)
ρ	Resistivity	(Ω.m)
ρ	Density	(kg / m^3)
σ_r	DC Rest Conductivity	(pS/m)
σ_{eff}	Effective conductivity	(pS/m)
τ	Relaxation time constant	(s)
ϕ	Potential	(V)
Φ	Fraction of stoichiometric fuel concentration	(dimensionless)
χ	Constant in Schon-type streaming current equation	($C.s.m^{-4}$)
Ω	Resistance	(Ohm)

Appendix A : Electrical Conductivities and Resistivities

Units of Bulk Conductivity and Resistivity

The *conductivity* (σ) is expressed in units of Siemen per meter (S/m), where the Siemen is the reciprocal Ohm. For liquids, conductivity units are frequently used (1 c.u. = 10^{-12} S/m = 1 pS/m = 10^{-14} $ohm^{-1}.cm.^{-1}$). Sometimes the quantity *resistivity* (ρ) is used. Conductivity and resistivity are related to the resistance "R" between the ends of a cylinder of material, of length "L" and cross-sectional area "A" by:

$$R = L/(\sigma \cdot A) = (\rho \cdot L)/A \quad (ohm) \qquad (A.1)$$

Resistivity is therefore simply the reciprocal of conductivity. In the case of solids, a special type of resistivity (surface resistivity) can be directly measured and is useful for estimating the rate at which surface charge will dissipate. This takes account of the fact that the surfaces of solids may be chemically and physically different from the bulk material, and may have surface treatments to change their electrical properties, such as topical antistatic agents.

Conductivity of Liquids

Conductivity provides a measure of the ease with which a flow of charge (current) will occur in a liquid in the presence of an electric field. For charged liquid entering a grounded container, the conductivity gives a measure of how fast the excess charge will flow to ground. Conductive liquids (σ nominally above 10^4 pS/m) have what can be termed "intrinsic" conductivity, and always contain positive and negative ions formed by molecular dissociation. In the presence of an electric field, for example in a conductivity cell, the positive ions (cations) will move to the negative terminal or cathode and the negative ions (anions) will move to the positive electrode or anode. This flow of ions represents a current in the liquid. Since ions are much larger than electrons, the resistance to motion is much larger than for electrons in a metal. The ionic velocity after initial acceleration in the field is:

Ionic velocity $v = \mu \cdot E$ (m/s) (A.2)

where μ = ionic mobility ($m^2.V^{-1}.s.^{-1}$)
E = electric field (V/m)

The current density $J = n \cdot q \cdot v$ ($A.m.^{-2}$) (A.3)

where n = ionic concentration per unit volume
q = ionic charge

Therefore the current density (current per unit area) is given by the product of the concentration of ions, the ionic charge, the ionic mobility and the electric field:

$$J = n \cdot q \cdot \mu \cdot E \quad (A.m.^{-2}) \qquad (A.4)$$

In practice several ionic species might be present and equation (A.4) could be summed for the individual (n, q, μ) values for the anions and cations present. For liquids obeying Ohm's Law, ($\phi = I \cdot R$) the conductivity may be written:

$$\sigma = J / E \qquad (\text{Ohm}^{-1}.\text{m}^{-1} \text{ or } \text{S.m.}^{-1}) \qquad (A.5)$$

Therefore the conductivity is proportional to the concentration and mobility of the ionic species present.

"Non-conductive" liquids (σ nominally below 50 pS/m) have what may be termed "extrinsic" conductivity and do not contain significant concentrations of ionic species when reasonably pure. They contain extremely small concentrations of charge carriers formed by cosmic rays and other processes, but in practice the measured conductivity derives mainly from impurities such as contaminants, additives, dissolved water and oxygen (plus their reaction products), and macroscopic charge carriers such as water droplets, gas bubbles and dust. The conductivity is especially dependent upon the amount of water absorbed from exposure to ambient air.

A third group of liquids (nominally 50 pS/m $< \sigma <$ 10^4 pS/m) may be termed "semiconductive". They either have a small amount of intrinsic conductivity or sufficient levels of contaminants or additives to render them weakly conductive. They are treated separately in this document because experiments show that during flow processes they can generate significant excess charge. However, their conductivity is normally sufficiently great to offset significant charge accumulation when they are loaded into grounded containers. This places them in a different category than "conductive" and "non-conductive" liquids. For example, the USAF have specified conductivities between 200-600 pS/m while 50 pS/m has been used as a "safe" level for civil aircraft. The higher values used by the USAF were introduced as a result of fires in plastic foam-filled tanks.

Ohmic Relaxation and Half-Value Times of Liquids

For a liquid-filled grounded container the degree of charge dissipation to the walls after some elapsed time in seconds is given by the equation:

$$Q_t = Q_o \bullet \exp(-t / \tau) \qquad (A.6)$$

where
Q_t = charge at time "t"
Q_o = initial charge
τ = relaxation time (s)

The *relaxation time* (τ) is a time constant related to conductivity by:

$$\tau = \varepsilon_o \bullet \varepsilon_o / \sigma \quad (s) \qquad (A.7)$$

where
ε_o = permittivity of free space (8.854×10^{-12} Farad/meter)
ε_r = dielectric constant of liquid
σ = conductivity (S/m)

From equation (A.6) it follows that the charge is reduced to (1 / e) of its initial value in one relaxation time. The *half-value time* ($t_{0.5}$) is the time taken for the charge to fall to one-half of its initial value. From equation (A.6) it follows that:

$$t_{0.5} = \tau \bullet \log_e 2 = 0.6931 \bullet \tau \qquad (A.8)$$

From equation (A.6) charge relaxes at an exponentially decreasing rate with time. In one relaxation time constant it falls to exp (-1) or 36.79% of its initial value. In two time constants it has fallen to 13.53%, in three to 4.98%, in four to 1.83% and in five to 0.67% of its initial value. These equations are commonly used to evaluate charge relaxation in filled or partly filled grounded containers. Often, hazardous charge can be assumed to relax to safe levels after three relaxation times in grounded equipment, after which approximately 5% of the initial charge remains.

Factors Affecting Ohmic Relaxation Times of Liquids

A conductivity value of 50 pS/m is often used to denote the maximum conductivity at which hazardous charges may accumulate in many items of grounded equipment. The relaxation behavior of liquids with such low conductivities can differ from that predicted from a measurement made in a standard conductivity test cell. The factors influencing relaxation behavior in practical situations are:

(1) type and concentration of impurities in the liquid differing from those in the test sample
(2) temperature different from that at which the test was made
(3) charge carrier type and concentration perturbed by charging process concerned
(4) relaxation behavior changed at conductivity less than about 1 pS/m

Conductivities and relaxation times can vary by many orders of magnitude (Appendix B). In the case of intrinsically conductive liquids it is possible to state that a liquid will always have a conductivity above some minimum value at a given temperature even at ultra-high purity. For non-conductive liquids such as hydrocarbons the conductivity can vary not only with temperature but also with trace amounts of impurities. A reduction in temperature generally causes a reduction in conductivity and this effect was estimated by Mason [4]:

$$\log_{10} (\kappa_2 / \kappa_1) \quad = \quad \alpha \cdot (T_2 - T_1) \qquad (A.9)$$

where for liquids such as gasoline and kerosine the constant "α" has a value of 0.015 K^{-1}. The application of this is that if a conductivity measurement in a test cell at 25 °C yields a value of 100 pS/m, the same liquid will have a conductivity of about 30 pS/m at -10 °C. The conductivity can therefore vary significantly with temperature and this effect should be allowed for when laboratory test data are appled to practical situations. For example, the conductivity could be measured at the lowest temperature anticipated under practical conditions.

At small values of conductivity, relaxation can be affected by the amount of excess charge, which changes the concentration or type of charge carrier present. Thus the term *effective conductivity* (σ_{eff}) is often used to describe the behavior of highly charged liquids, while the term *rest conductivity* (σ_r) is used to denote the value measured for the quiescent liquid in a test cell. As discussed in [5] the effective conductivity of highly charged liquids with rest conductivity above 1 pS/m can be as low as one-fourth the value measured in a test cell. BP reported [8] that the effective conductivity could be as little as one-tenth the rest conductivity but on average one-half. Conversely, liquids with rest conductivities less than about 1 pS/m relax faster than predicted from the Ohmic relaxation time.

Hyperbolic Relaxation at Conductivities less than about 1 pS/m

As discussed in [2], the ohmic relaxation behavior predicted by equation (A.6) is not followed if σ_r is less than about 2 pS/m. Instead the charge relaxes faster and follows a

hyperbolic rather than an exponential law. The integrated rate equation does not contain a conductivity term but depends on the initial charge density and charge carrier mobility:

$$S_t = S_0 / [1 + \mu \cdot S_0 \cdot t / (\varepsilon_0 \cdot \varepsilon_r)] \qquad (A.10)$$

where the measured charge carrier mobility "μ" is about 1 x 10^{-8} $m^2.V^{-1}.s.^{-1}$ and S is the charge density in Coulombs per cubic meter. To be equivalent to a criterion of "three relaxation times" for charged liquid to relax to non-hazardous levels, the ratio S_t / S_0 should be 0.05. Rearranging (10) and substituting for "μ" and "ε_0" gives:

$$t = 0.0168 \cdot \varepsilon_r / S_0 \quad (s) \qquad (A.11)$$

Table A.1 shows the dissipation times to reduce the charge density to 5% of the initial values for a series of charge densities (S_0) and for liquid dielectric constants varying from 2 to 4. Also shown are the dissipation times needed to achieve 20 and 30 $\mu C/m^3$ (the respective threshold hazardous charge densities [8, 85] for bottom filling and top filling tank cars and trucks).

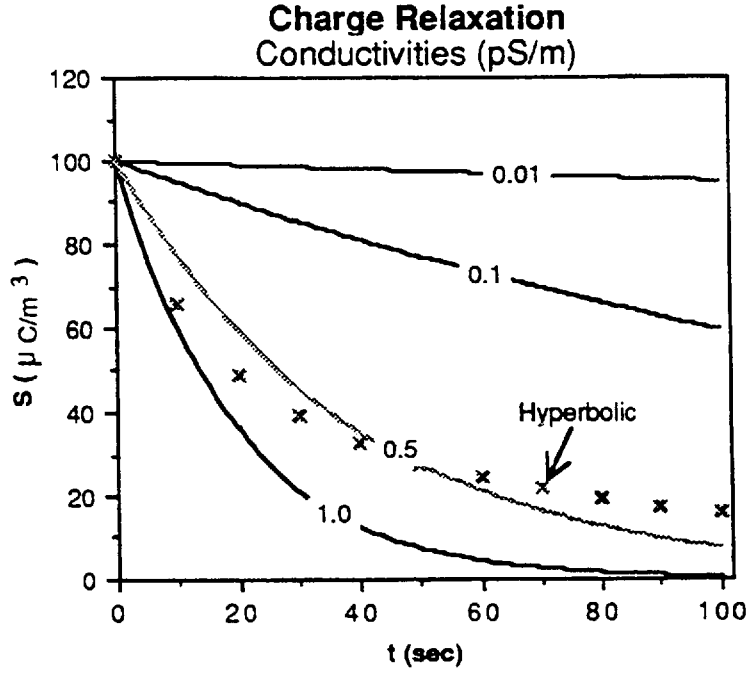
Table A.1 : Charge Dissipation Times for Hyperbolic Relaxation (ε_r = 2-4)

S_0 ($\mu C/m^3$)	Time (s) to 5% of S_0	Time (s) to 20 $\mu C/m^3$	Time (s) to 30 $\mu C/m^3$
5000	7-13	88 - 176	59 - 118
2000	17-34	87 - 175	58 - 117
1500	22-45	87 - 175	58 - 116
1000	34-67	87 - 174	57 - 114
500	67-134	85 - 170	55 - 111
100	336-672	71 - 142	41 - 82

For most hydrocarbon liquids, dielectric constants are closer to 2 than to 4, and the dissipation time is proportional to ε_r. To obtain the same fraction of initial charge density as would be provided by 3 relaxation times of a liquid which relaxes exponentially, a single charge dissipation time of 100 seconds should cover all important cases plus provide the greatest margin for safety at the highest initial charge densities. Also, it is seen that in order to reduce the charge density to a safe level (20 - 30 $\mu C/m^3$), the magnitude of the initial charge density above about 100 $\mu C/m^3$ is unimportant for hyperbolic relaxation. The same dissipation time is needed in each case. The result is significant in relation to filter placement upstream of non-inerted containers. It is often argued that charging at low conductivities is much reduced and compensates for long charge dissipation times. However, it can be seen that to achieve safe charge density levels (20 - 30 $\mu C/m^3$) for tank filling, such a margin of safety does not exist and about 100 seconds of relaxation is still required. Bustin [2] showed that charge densities could exceed 500 $\mu C/m$ downstream of filters even at conductivities in the range 0.01 pS/m.

Figure A.1 shows hyperbolic relaxation from an initial charge density of 100 $\mu C/m^3$, compared with exponential relaxation at a series of conductivities. It is seen that for short periods of relaxation, such as the filling time for a drum, hyperbolic relaxation is similar to that of exponential relaxation at an effective conductivity of 0.5 pS/m. However, for longer time scales, hyperbolic relaxation is slower. The large errors that would occur if exponential relaxation were assumed to hold at low conductivities (0.1 pS/m etc) is apparent.

Figure A.1 : Exponential and Hyperbolic Relaxation in a Grounded Metal Container [7]



Conductive, Semiconductive and Non-Conductive Liquids

Liquids can often be categorized by inspection into those which are intrinsically "conductive" and those which are intrinsically "non-conductive". The former have conductivities greater than 10^4 pS/m regardless of purity. The latter have conductivities less than 50 pS/m when reasonably pure. Appendix B shows a listing of liquids falling into these categories. Also shown is a group of "semiconductive" liquids which have intermediate conductivities. This group includes intrinsically non-conductive liquids such as hydrocarbons containing small quantities of conductive additives.

Intrinsically conductive liquids ($\sigma > 10^4$ pS/m) are always conductive, irrespective of purity. They include most acids, alcohols, aldehydes, amines, epoxides, esters, glycols, glycol ethers, ketones, nitriles, peroxides and other materials usually having a polar character (dielectric constant greater than about 5). They may be hazardous in terms of flammability and ignition energy, and some may be readily ignited by static discharges, although the liquids rapidly lose excess charge in grounded equipment.

Intrinsically non-conductive liquids are conductive (or semiconductive) only when they contain conductive additives or contaminants. Non-conductors include aliphatic, aromatic and cyclic hydrocarbons, carbon disulfide, simple ethers, some halocarbons, some higher acids and their esters and some silicon-based materials (such as silanes). Dielectric constants are usually less than about 4. Most petroleum distillates fall into this group, although commercial blends such as gasolines often contain additives that render them semiconductive. Heavier petroleum fractions tend to have larger conductivities, partly due to the presence of contaminants. Crude oils and most black oils, for example, have conductivities above 1000 pS/m and relaxation times of less than 0.02 seconds. They fall either into "conductive" or "semiconductive" categories.

Liquids displaying some of the characteristics of both groups, such as substituted hydrocarbons containing other atoms or functional groups, may be difficult to categorize by simple inspection and measurement should be made. They may fall into the "semiconductive" category.

Some materials which are normally conductive may become good insulators when they solidify. This may create hazards in equipment where the solidified material prevents liquid contact with grounded surfaces. Luttgens [9] describes a biphenyl fire involving this mechanism.

Non-conductive liquids are most likely to generate and accumulate charge. Semiconductive liquids generate charge during flow but owing to their smaller relaxation times are less likely to accumulate charge when a grounded container is being filled. Conductive liquids do not usually represent a static hazard when handled in grounded equipment, but may carry charge when sprayed or when handled in plastic equipment.

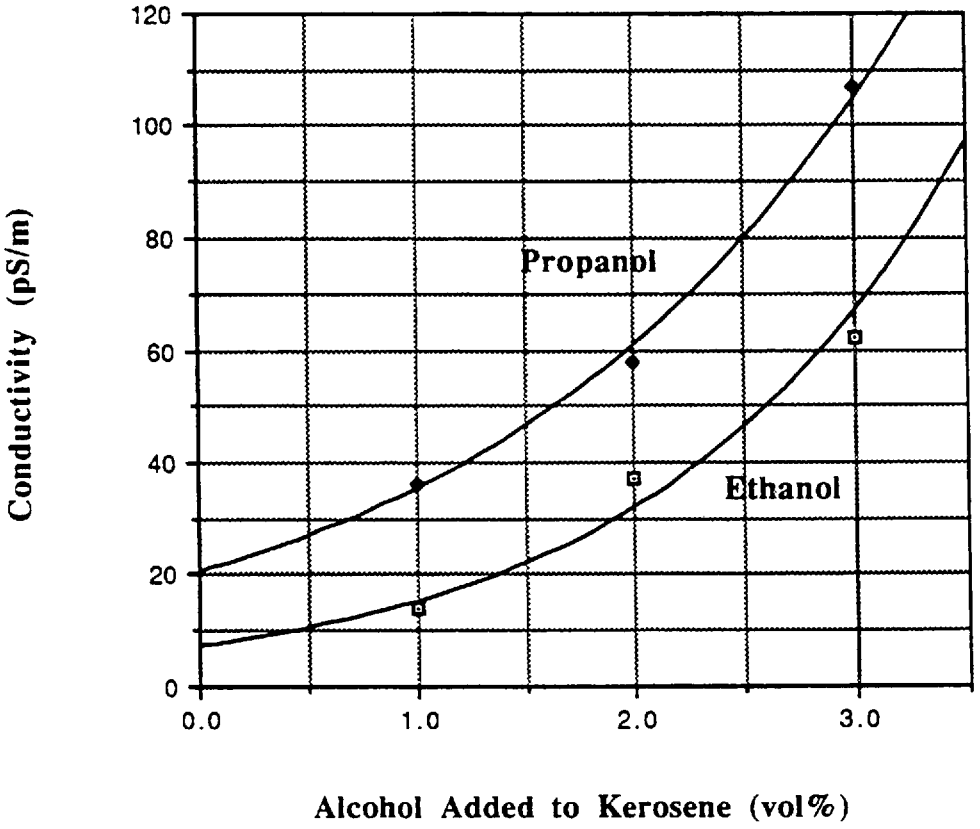
Appendix B shows a compilation of liquid conductivities, dielectric constants, and relaxation times. Conductivities (and relaxation times) given are representative values only and may vary as described above. No relaxation times are given for liquids whose listed conductivities are less than 2 pS/m, since as discussed above the relaxation time is not a meaningful concept for these liquids and they are found to dissipate charge at a faster rate. They are assigned instead a "dissipation time" of approximately 100 seconds.

Theories for Electrical Conductivity

Antistatic Additives

Figure A.2 adapted from [36] shows the effect of adding alcohols to white kerosene having a nominal conductivity of about 10 pS/m (in the Figure it is assumed to be 14±6 pS/m). It is seen that the conductivity is raised above 50 pS/m upon addition of a few percent by volume of alcohol but that these levels are insufficient to render it conductive. The importance of this is that it is not practical to use conductive liquids like alcohols as antistatic additives for mass-produced fuels such as kerosene and gasoline (where a few parts per million of antistatic agent is required). However, the method offers a solution for some solvent mixtures where (for example) non-conductive heptane might be blended with a large amount of methyl ethyl ketone or other conductive solvent. Note that the variation of conductivity is not exponential as suggested by Figure A.2, since at 100% alcohol the respective conductivities of propanol and ethanol are only 135000 and 917000 pS/m. It is possible the relationship will be S-shaped.

Figure A.2 : Effect of Alcohol Addition on Conductivity of Kerosene



Charge Neutralization

Charge neutralization is an alternative to the use of antistatic additives. The two broad types are passive neutralizers (where neutralization is produced as a result of the electric field produced by the charged liquid at sharp electrodes in the liquid) and active neutralizers (where high alternating or direct voltages are applied to sharp electrodes in the liquid, with or without control feedback from a downstream sensor).

(1) Passive Charge Neutralization

In exponential (Ohmic) relaxation theory the relaxation rate is independent of geometry and it is not predicted that passive neutralizers (which typically comprise grounded needles protruding from the inner pipe wall) will be effective. However, such devices have been shown to work and have been marketed. At very high values of electric field such as at the tips of needles or blades, ionization occurs allowing charge injection or absorption to or from the liquid.

A.O. Smith Static Charge Reducer (SCR)

Ciotti [27] presented development work of the SCR which A.O. Smith was producing under license by Standard Oil of Indiana. A design description [28] was as follows. A three foot length of ten inch pipe was fitted with a two inch thick HDPE liner giving a six inch effective id. Sixteen sharply pointed electrodes were screwed through the pipe wall to protrude into the liquid flow. Electrically, the principle of operation was due to the action of the polyethylene liner in producing a high voltage capacitor at the wall, the inner plate being the layer of charged liquid. Without the liner, the device would not operate since the potential difference between the needles and the wall would only be that due to the potential gradient through the liquid. The device would not work effectively until the wall capacitor had charged up due to charged liquid flow.

The device was designed to limit effluent charge density to below 30 $\mu C/m^3$ with line sizes of 3, 4, and 6 inch and flow rates up to 1200 gpm. 30 $\mu C/m^3$ was the "safe" level held at the time for tank trucks based on the work of Ginsburgh et al [29]. The average time taken to charge the wall capacitor was 20 seconds.

Testing of the SCR

Tests were made [27] with kerosene of "relaxation time" 30-538 seconds. Assuming the quoted relaxation times in [27] to be based on exponential relaxation theory, the rest conductivities were therefore in the range 0.03 - 0.6 pS/m for a nominal $\varepsilon_r = 2.0$. From the above discussion, hyperbolic relaxation would be expected in this range of rest conductivites. Tests reported in [27] for kerosene with a "relaxation time " of 264 seconds ($\sigma = 0.07$ pS/m) in terms of charge density "S" in $\mu C/m^3$ were:

S (inlet)	S (outlet) @ 400 gpm	@800 gpm	@1200 gpm
160	8	6	-
160	4	-	-
175	-	-	12
180	4	6	-
185	-	6	12
195	4	-	10
200	0	4	9
210	-	6	9
217	0	-	-
220	0	6	-
235	-	-	9
240	-	4	8

All of these outlet charge densities were less than 13 $\mu C/m^3$, well below the hazardous threshold of 20 - 30 $\mu C/m^3$ for tanker filling.

Industry Experience of A.O. Smith SCR

Despite the promising work described above, the SCR is no longer manufactured and few devices remain in service. This disappointing outcome was due to the formation of a relatively conductive layer on the inside surface of the polyethylene, which derived from the petroleum product being handled. Deposition may have been due partly to the operation of the device. In any case, the layer prevented the formation of large internal potentials and efficiency fell off with use.

In practice, this meant that the devices had to be periodically removed for cleaning. In order to ascertain when service was needed, it was necessary to use a downstream charge density monitor which unlike the SCR has moving parts and is relatively expensive. Another reason for the demise of the SCR is that in the 1970s the use of antistatic additives became widespread in the petroleum industry. It is possible that the SCR would be beneficial in fine chemical service (benzene, toluene etc) where antistatic additives cannot be used. It is possible that the deposition problem experienced with petroleum fractions would not occur in these cases.

A.O. Smith Charge Density Meter

Few of these devices are in use today but they have been used in several research projects and a particular problem should be noted. The meter is a rotating vane type. It is inserted some distance radially from a fitted tee holding the motor and instrument body so that the sensing surface is in the flow. Unlike a flush wall mounted sensor, calibration for this geometry (proportionality between charge density and electric field) is not simple. The device is set up to sample the field due to a squat cylinder of charged liquid defined by a one-ended cylindrical metal attachment with holes in it (one design resembled a vacuum tube cover). Hence, the sensor looks into the end of this cylinder of liquid which is surrounded by the grounded metal surface. A calibration was supplied for the instrument based on the theoretical field-charge density relationship.

The problem with the design is that as the liquid passes into the sample volume through the holes, it gets charged up. The charging increases with flow velocity. Unless this charge is small compared with the charge density generated upstream, the reading is wrong. A calibration curve could be generated using an isolated metal receiving tank downstream to act as a Faraday Pail, but the limitation due to charging on the sample screen may be sensitive to the particular charging tendency of the liquid in addition to flow rate. Therefore this type of charge sensor is accurate only for high values of charge density such as downstream of a filter.

(2) Active Charge Neutralization

To avoid the practical difficulties of the SCR a device was developed [35] using active charge neutralization plus a downstream charge density monitor having no moving parts. The principle of operation was that charge density would be sensed in a downstream relaxation chamber and the information fed back to a charge injector comprising a chamber containing sharp blades. The blades were supplied with positive or negative DC current using the downstream monitor as a null detector. The use of active injection at about 25 kV meant that no internal capacitor was required as in the SCR. However, it is possible that the internal HV spark plug insulators would ultimately cause excessive currents to be drawn should deposition occur as in the SCR. The principal problems with the device were (apart from cost and complexity):

(1) The USAF found that the blade injectors could fall off, possibly following "singing" in the flow.

(2) To allow for effective conductivity effects it would be necessary to use two downstream charge density monitors and at low conductivity values it was doubtful whether there would be sufficient relaxation even with a large separation between the monitors. The calibration made for the charge density monitors neglected hyperbolic relaxation at low conductivity values and was based solely upon exponential relaxation theory.

(3) There were concerns about providing intrinsic safety for use in flammable atmospheres.

The use of antistatic additives was prevalent at the time this device was developed and interest was correspondingly low.

Passive Devices for Potential Reduction

Potentials can be reduced by inserting grounded rods, baffle plates or other conductive surfaces into a tank. The presence of baffle plates and dip tubes in tankers serve to reduce the liquid surface and space potentials. The effect is most readily modeled using finite element computer methods such as "THREE D" [40].

Resistivities of Solids

Criteria for Antistatic and Conductive Solids

Appendix B : Typical Conductivities, Dielectric Constants and Relaxation (or Dissipation) Times

Liquid	σ (pS/m)	ε_r	τ (s)
	conductive liquids ($\sigma > 10^4$ pS/m)		
acetaldehyde (15°C)	1.7×10^8	21.1	1.1×10^{-6}
acetamide	8.8×10^7	59	5.9×10^{-6}
acetic acid (0°C)	5×10^5	6.15	1.1×10^{-4}
acetic anhydride (25°C)	4.8×10^7	n/a	n/a
acetone (25°C)	6×10^6	20.7	3×10^{-5}
acetonitrile (20°C)	7×10^8	37.5	5×10^{-7}
acetophenone (25°C)	3.1×10^5	17.39	5.0×10^{-4}
acetyl bromide (25°C)	2.4×10^8	n/a	n/a
acetyl chloride (25°C)	4×10^7	n/a	n/a
acrolein	1.55×10^7	n/a	n/a
acrylonitrile	7×10^5	38	4.8×10^{-4}
allyl alcohol (25°C)	7×10^8	n/a	n/a
aminoethylethanolamine**	$> 1 \times 10^6$	n/a	n/a
n-aminoethyl piperazine**	2.4×10^5	n/a	n/a
ammonia (-79°C)	1.3×10^7	n/a	n/a
amyl acetate	1.6×10^5	4.75	2.6×10^{-4}
aniline (25°C)	2.4×10^6	6.89	2.5×10^{-5}
arsenic tribromide (25°C)	1.5×10^8	n/a	n/a
arsenic trichloride (25°C)	1.2×10^8	n/a	n/a
benzaldehyde (25°C)	1.5×10^7	n/a	n/a
benzoic acid (125°C)	3×10^5	n/a	n/a
benzonitrile (25°C)	5×10^6	25.2	4.5×10^{-5}
benzyl alcohol (25°C)	1.8×10^8	n/a	n/a
benzyl cyanide	$<5 \times 10^6$	18.7	$>3.3 \times 10^{-5}$
biphenyl (liquid: above 120°C)	$>1 \times 10^4$	n/a	n/a
bromoform (tribromomethane) (25°C)	$<2 \times 10^6$	4.39	$>1.9 \times 10^{-5}$
iso-butyl acetate	2.55×10^{10}	5.29	1.8×10^{-9}
iso-butyl alcohol	9.12×10^5	17.51	1.7×10^{-4}
sec-butyl alcohol	$<1 \times 10^7$	16.56	$>1.5 \times 10^{-5}$
tert-butyl alcohol	2.66×10^6	12.47	4.2×10^{-5}
butyl CARBITOL**	$>1 \times 10^6$	n/a	n/a
iso-butyl chloride	1×10^4	6.49	5.7×10^{-3}
sec-butyl chloride	1×10^4	7.09	6.3×10^{-3}
capronitrile (25°C)	3.7×10^8	n/a	n/a
m-chloroaniline (25°C)	5×10^6	n/a	n/a
m-cresol	1.397×10^6	11.8	7.5×10^{-5}
o-cresol	1.27×10^5	11.5	8.0×10^{-4}
p-cresol	1.378×10^6	9.91	6.4×10^{-5}
cyanogen	$<7 \times 10^5$	n/a	n/a
cyclohexanone	5×10^5	n/a	n/a
cymene (25°C)	$<2 \times 10^6$	n/a	n/a
dibutyl-o-phthalate	1.8×10^5	6.436	3.2×10^{-4}
dichloroacetic acid (25°C)	7×10^6	n/a	n/a
cis-dichloroethylene	8.5×10^5	9.20	9.6×10^{-5}
dichlorohydrin (25°C)	1.2×10^9	n/a	n/a

diethylamine (-33.5°C)	2.2×10^{5}	n/a	n/a
diethyl carbonate (25°C)	1.7×10^{6}	2.82	1.5×10^{-5}
diethylene glycol	5.86×10^{7}	31.69	4.8×10^{-6}
diethylenetriamine**	$>1 \times 10^{6}$	n/a	n/a
diethyl oxalate (25°C)	7.6×10^{7}	n/a	n/a
diethyl sulfate (25°C)	2.6×10^{7}	n/a	n/a
dimethyl acetamide	1.1×10^{7}	n/a	n/a
dimethyl formamide	6×10^{6}	36.71	5.4×10^{-5}
dimethyl sulfate (0°C)	1.6×10^{7}	n/a	n/a
dimethyl sulfoxide	2×10^{5}	46.68	2.1×10^{-3}
diphenyl oxide	$<1.7 \times 10^{6}$	4.22	$>2.2 \times 10^{-5}$
epichlorohydrin (25°C)	3.4×10^{6}	22.6	5.9×10^{-5}
ethanolamine	1.1×10^{9}	37.72	3.0×10^{-7}
ethyl acetate (25°C)	$<1 \times 10^{5}$	6.02	$>5.3 \times 10^{-4}$
ethyl acetoacetate (25°C)	4×10^{6}	15.7	3.5×10^{-5}
ethyl acrylate**	3.35×10^{5}	n/a	n/a
ethyl alcohol (25°C)	1.35×10^{5}	24.55	1.6×10^{-3}
ethylamine (0°C)	4×10^{7}	n/a	n/a
ethyl benzoate (25°C)	$<1 \times 10^{5}$	6.02	$>5.3 \times 10^{-4}$
ethyl bromide (25°C)	$<2 \times 10^{6}$	9.39	$>4.2 \times 10^{-5}$
ethyl chloride	$<3 \times 10^{5}$	9.45	$>2.8 \times 10^{-4}$
ethyl cyanoacetate	6.9×10^{7}	26.7	3.4×10^{-6}
ethylene carbonate	$<1 \times 10^{7}$	89.6	$>7.9 \times 10^{-5}$
ethylenediamine	9×10^{6}	12.9	1.3×10^{-5}
ethylene dibromide (25°C)	$<2 \times 10^{4}$	4.78	$>2.1 \times 10^{-3}$
ethylene dichloride (25°C)	3×10^{6}	n/a	n/a
ethylene glycol	1.16×10^{8}	37.7	2.9×10^{-6}
ethylene glycol monobutyl ether	4.32×10^{7}	9.30	1.9×10^{-6}
ethylene glycol monoethyl ether	9.3×10^{6}	29.6	2.8×10^{-5}
ethylene glycol monomethyl ether	1.09×10^{8}	16.93	1.4×10^{-6}
ethyleneimine	8×10^{8}	18.3	2.0×10^{-7}
ethylene oxide	4×10^{6}	12.7	2.8×10^{-5}
ethyl formate	1.45×10^{5}	7.16	4.4×10^{-4}
ethylidene chloride	2.0×10^{5}	10.0	4.4×10^{-4}
ethyl isothiocyanate (25°C)	1.26×10^{7}	n/a	n/a
ethyl lactate	1.0×10^{8}	13.1	1.2×10^{-6}
ethyl nitrate (25°C)	5.3×10^{7}	n/a	n/a
ethyl oxalate	7.12×10^{7}	1.8 (sic)	2.2×10^{-7}
ethyl propionate	8.33×10^{10}	5.65	6×10^{-10}
ethyl thiocyanate (25°C)	1.2×10^{8}	n/a	n/a
eugenol (25°C)	$<1.7 \times 10^{6}$	n/a	n/a
formamide (25°C)	4×10^{8}	111.0	2×10^{-6}
formic acid (25°C)	6.4×10^{9}	58.5	8.1×10^{-8}
furfural (25°C)	1.5×10^{8}	n/a	n/a
glycerol (25°C)	6.4×10^{6}	42.5	5.9×10^{-5}
guaiacol (25°C)	2.8×10^{7}	n/a	n/a
hydrogen bromide (-80°C)	8×10^{5}	n/a	n/a
hydrogen chloride (-96°C)	1×10^{6}	n/a	n/a
hydrogen iodide (@b.p.)	2×10^{7}	n/a	n/a
iodine (110°C)	1.3×10^{4}	n/a	n/a
mercury (0°C)	1.063×10^{18}	n/a	n/a
methoxy triglycol**	$>1 \times 10^{6}$	n/a	n/a
methyl acetamide	2×10^{7}	191.3	8.5×10^{-5}

methyl acetate (25°C)	3.4×10^{8}	6.68	1.7×10^{-7}
methyl alcohol (18°C)	4.4×10^{7}	32.70	6.6×10^{-6}
methyl cyanoacetate	4.49×10^{7}	29.30	5.8×10^{-6}
methyl ethyl ketone (25°C)	1×10^{7}	18.51	1.6×10^{-5}
methyl formamide	8×10^{7}	182.4	2.0×10^{-5}
methyl formate	1.92×10^{8}	8.5	3.9×10^{-7}
methyl iodide (25°C)	$<2 \times 10^{6}$	n/a	n/a
methyl isobutyl ketone	$<5.2 \times 10^{6}$	13.11	$> 2.2 \times 10^{-5}$
methyl nitrate (25°C)	4.5×10^{8}	n/a	n/a
n-methyl-2-pyrrolidone	2×10^{6}	32.0	1.4×10^{-4}
naphthalene (82°C)	4×10^{4}	n/a	n/a
nitrobenzene (0°C)	5×10^{5}	34.82	6.2×10^{-4}
nitroethane	5×10^{7}	28.06	5.0×10^{-6}
nitromethane (18°C)	6×10^{7}	35.87	5.3×10^{-6}
1-nitropropane	3.3×10^{7}	23.24	6.2×10^{-6}
2-nitropropane	5×10^{7}	25.52	4.5×10^{-6}
o- or m-nitrotoluene (25°C)	$<2 \times 10^{7}$	n/a	n/a
octyl alcohol	1.39×10^{7}	10.34	6.9×10^{-6}
phenol	1×10^{6}	9.78	8.7×10^{-5}
phenyl isothiocyanate (25°C)	1.4×10^{8}	n/a	n/a
phosgene (25°C)	7×10^{5}	n/a	n/a
polyalkylene oxide (Y-6132)**	$> 1 \times 10^{7}$	n/a	n/a
polyalkylene oxide (Y-6854)**	5.4×10^{5}	n/a	n/a
propionaldehyde (25°C)	8.5×10^{7}	18.5	1.9×10^{-6}
propionic acid (25°C)	$<1 \times 10^{5}$	3.44	$>3.0 \times 10^{-4}$
propionitrile	8.51×10^{6}	27.2	2.8×10^{-5}
propyl acetate	2.2×10^{7}	6.002	2.4×10^{-6}
n-propyl alcohol (25°C)	2×10^{6}	20.33	9×10^{-5}
iso-propyl alcohol (25°C)	3.5×10^{8}	19.92	5×10^{-7}
propyl formate	5.5×10^{9}	7.72	1.2×10^{-8}
propyl PROPASOL**	$>1 \times 10^{6}$	n/a	n/a
pyridine (25°C)	5.3×10^{6}	12.4	2.1×10^{-5}
quinoline (25°C)	2.2×10^{6}	9.00	3.6×10^{-5}
salicyaldehyde (25°C)	1.6×10^{7}	13.9	7.5×10^{-6}
succinonitrile	5.64×10^{10}	56.5	8.9×10^{-9}
sulfolane (tetramethylene sulfone)	$<2 \times 10^{6}$	43.3	$>1.9 \times 10^{-4}$
sulfonyl chloride (25°C)	2×10^{8}	n/a	n/a
sulfuric acid (25°C)	1×10^{12}	n/a	n/a
tetraethylenepentamine**	$>1 \times 10^{6}$	n/a	n/a
tetramethylurea	$<6 \times 10^{6}$	23.06	$>3.4 \times 10^{-5}$
m-toluidine	5.5×10^{4}	9.91	1.6×10^{-3}
o-toluidine	3.79×10^{7}	6.34	1.5×10^{-6}
p-toluidine (100°C)	6.2×10^{6}	4.98	7.1×10^{-6}
trichloroacetic acid (25°C)	3×10^{5}	n/a	n/a
1,1,1-trichloroethane (?)	7.3×10^{5}	7.53	9.1×10^{-5}
triethylene glycol	8.4×10^{6}	23.69	2.5×10^{-5}
triethylenetetramine**	$>1 \times 10^{6}$	n/a	n/a
trimethylamine (-34°C)	2.2×10^{4}	n/a	n/a
water (extremely pure)	4.3×10^{6}	80.4	1.7×10^{-4}
water (air distilled)	$\sim 1 \times 10^{9}$	80.4	7.1×10^{-7}

semiconductive liquids ($50 < \sigma < 10^4$ pS/m)

armeen**	470	n/a	n/a
biphenyl (liquid @ 69-120°C)	2500-10000	n/a	n/a
bromobenzene	1200	5.40	4×10^{-2}
1-bromonaphthalene	3660	4.83	1.1×10^{-2}
butyl acrylate**	3580	n/a	n/a
chlorobenzene	7000	5.621	7.1×10^{-3}
chloroform	<10000	4.806	$>4.3 \times 10^{-3}$
dibutyl sebacate	1700	4.54	2.4×10^{-2}
o-dichlorobenzene	3000	9.93	2.9×10^{-3}
ethylene dichloride	4000	10.36	2.2×10^{-2}
2-ethylhexyl acrylate**	610	n/a	n/a
gasoline (leaded)	>50	2.3	<0.41
hydrogen sulfide (@ b.p.)	1000	n/a	n/a
methylene chloride	4300	8.93	1.8×10^{-2}
pentachloroethane*	100	3.83	0.34
1,2,4-trichlorobenzene*	200	4.08	0.18
trichloroethylene	800	3.42	3.7×10^{-2}
vinyltrimethoxysilane (<2% CH_3OH)	5900	n/a	n/a

non-conductive liquids ($\sigma < 50$ pS/m)

anisole (methyl phenyl ether)	10	4.33	3.8
benzene (purified)	5×10^{-3}	2.3	~100 (dissipation)
biphenyl (solid: less than 69°C)	0.17	n/a	not applicable
bromine (17°C)	13	n/a	n/a
butyl stearate	21	3.111	1.3
caprylic acid (octanoic acid)	<37	2.45	>0.58
carbon disulfide (1°C)	7.8×10^{-4}	2.6	~100 (dissipation)
carbon tetrachloride	4×10^{-4}	2.238	~ 100 (dissipation)
chlorine (-70°C)	<0.01	n/a	n/a
cyclohexane	<2	2.0	>8.8
decalin*	6	2.18	3.2
dichlorosilane	n/a	n/a	n/a
diesel oil (purified)	~ 0.1	~ 2	~100 (dissipation)
diethyl ether	30	4.6	1.4
1,4-dioxane (diethylene oxide)	0.1	2.2	~100 (dissipation)
ethyl benzene	30	2.3	0.68
gasoline (straight run)	~ 0.1	~2	~100 (dissipation)
heptane (purified)	3×10^{-2}	2.0	~100 (dissipation)
hexane (purified)	1×10^{-5}	1.90	~100 (dissipation)
hexamethyldisilazane	29	n/a	n/a
isovaleric acid	<40	2.64	>0.58
jet fuel	0.01 - 50	2.2	0.39 - 100
kerosene	1 - 50	2.2	0.39 - 19
pentachlorodiphenyl*	0.8	5.06	~100 (dissipation)
SiH fluid (Y-10354)**	2.5	n/a	n/a
silicon tetrachloride	n/a	n/a	n/a
styrene monomer	10	2.43	2.2
sulfur (115°C)	100	n/a	n/a
toluene	1	2.38	21
trichlorosilane	n/a	n/a	n/a
turpentine	22	n/a	n/a
iso-valeric acid (80°C)	<40	n/a	n/a
xylene	0.1	2.38	~100 (dissipation)

Sources for Appendix B

[a] Britton, L.G., and Smith, J.A., "Static Hazards of Drum Filling, Part I : Actual Incidents and Guidelines", Plant/Operations Progress, Vol. 7, No. 1 (January 1988).

[b] Berufsgenossenschaft der Chemischen Industrie, Statische Elektrizitat, Richt. Nr. 4, Aug 4 (1980).

[c] Luttgens, G., "Collection of Accidents Caused by Static Electricity", J. Electrostatics, 16 (1985) pp. 247-255.

[d] Hill, N.E., et al., "Dielectric Properties and Molecular Behavior", Van Nostrand Co., NY (1969).

[e] Dean, J.A. (Editor), "Lange's Handbook of Chemistry", 13th Ed., McGraw-Hill, New York.

Notes : Reference [b] was the principal source of data, taken from the original German, although [e] was the preferred source. As cautioned in [b], the data should be regarded as approximate only, since they derive from various authors under different experimental conditions (particularly liquid purity and temperature). In the case of non-conductive liquids especially, the conductivity of highly purified material may be much less than indicated in Table A-1. Almost all light hydrocarbons (aliphatic, cyclic and aromatic) fall into the "non-conductive" category when reasonably pure. Note that temperature changes and especially phase transitions (see biphenyl) can change the conductivity category. Liquids marked with an asterisk are assigned data from ref [d]. Two asterisks denote data measured at a Union Carbide Plant. Suspect data are indicated "?".

Measurement of Conductivity

APPENDIX C : MINIMUM IGNITION ENERGIES OF GASES AND MISTS

Minimum Ignition Energies of Gases

Techniques for the measurement of minimum ignition energies of gases in oxidants such as air or oxygen have been well established and a standard method [13] is described in ASTM E 582-76 "Standard Test Method for Minimum Ignition Energy and Quenching Distance in Gaseous Mixtures". In all cases it is found that the minimum spark energy needed to cause ignition (MIE) attains a lowest value somewhere near the middle of the flammable range and (by definition) approaches infinity at the lower and upper flammability limits. Thus, a plot of minimum ignition energy against gas concentration in the oxidant follows a U-shaped curve (resembling the gamma function) from which the lowest MIE value can be found.

As discussed in [59] the MIE is greatly affected by the test equipment used. Variables such as electrode material and geometry, spark circuit capacitance and other parameters determine the value of MIE found. In principle all the variables known to affect MIE should be optimized to determine the "lowest minimum ignition energy" (LMIE). However, in practice standard methods such as [13] are used and these do not independently optimize all the variables. Data from [59] show that when this is done, the LMIEs found can be less than those determined using standard methods. In particular, for simple capacitance sparks the MIE is decreased as storage capacitance is decreased and as electrode tip diameter is decreased. An "absolute" LMIE is limited by the ability of metal surfaces to hold charge (maximum 2.7 nC/cm^2), since the capacitors used at very low energies are effectively isolated spheres. Also, at high potentials ionization begins to be a problem for pointed electrodes.

Table C-1 [59] shows how the MIE (mJ) of 28 vol% hydrogen and 8.5 vol% methane in air varied with capacitance (pF) and electrode diameter (mm). "Points" refers to the use of steel gramophone needles. This Table shows how MIE is decreased with decreased capacitance and electrode diameter up to the experimental limits discussed.

Table C-1 : MIE Variation with Capacitance and Electrode Diameter

		Minimum Ignition Energy (mJ) at Electrode Diameter			
Fuel	pF	15 mm	1.59 mm	0.5 mm	Points
Hydrogen	146	0.390	0.260	0.210	0.073
	50	n/a	0.160	n/a	n/a
	30	0.094	0.079	n/a	0.034
	6.1	0.022	**0.016**	0.019	n/a
Methane	146	4.67	2.21	2.09	0.75
	50	n/a	1.06	n/a	n/a
	30	0.94	0.87	n/a	n/a
	13	n/a	0.40	n/a	n/a
	6.1	**0.21**	n/a	n/a	n/a

Table C-2 [59] shows the minimum voltage across the spark gap needed to ignite the optimum hydrogen and methane mixtures in air. It shows that at small capacitance, at least 1000 volts is needed for hydrogen and at least 3200 volts for methane. These minima increase with increased electrode diameter and with decreased storage capacitance. It should be noted that 146 pF is typical for the capacitance of a person, steel drums may have capacitances in the 30-50 pF range, and a road tanker may have a capacitance of around 1000 pF.

Table C-2 : Minimum Ignition Voltage Variation with Capacitance and Electrode Diameter

Fuel	pF	Minimum Ignition Voltage (V) at Electrode Diameter 15 mm	1.59 mm	0.5 mm	Points
Hydrogen	146	2300	1900	1700	**1000**
	50	n/a	2500	n/a	n/a
	30	2500	2300	n/a	1500
	6.1	2700	2300	2500	n/a
Methane	146	8000	5500	5350	**3200**
	50	n/a	6500	n/a	n/a
	30	7900	7600	n/a	n/a
	6.1	8300	n/a	n/a	n/a

Table C-3 gives lowest reported minimum ignition energies (LMIE values) for combustible gases in air and other oxidants, nominally at atmospheric temperature and pressure. These values were obtained using standard methods and were found in various literature sources. It should be noted that MIEs generally decrease with increased temperature, pressure and oxidant concentration. In the literature, the term "MIE" is commonly used to denote LMIE.

Spark Duration

The ASTM method [13] does not allow spark characteristics to be independently varied. The energy contained in a storage capacitor is discharged extremely rapidly (timeframe ~1 μs) into a spark gap through a spark circuit having minimal inductance. Care is taken to account for all stray capacitance in the spark circuit. For most combustible gas mixtures with an oxidant the ASTM method has been found [13] to give LMIEs that are as low as, or lower than, those obtained using other methods. Also, it should be appreciated that practically all "static" sparks from conductors are simple capacitive sparks of the type used in the ASTM test. Some studies have found [2] that for very short duration sparks a large fraction of the stored energy is radiated away as a shock wave, and extended spark durations of the order 100 μs were found to be optimum. The optimum spark duration may depend on flow velocity, pressure and the gas mixture concerned. For flames of very small burning velocity such as ethylene oxide decomposition flames, an extended spark duration may be necessary owing to the slow rate at which the flame kernel attains its minimum size for self-propagation. In order to address any effects of spark characteristics on gas MIE the equipment and technique need to be far more sophisticated than that described by ASTM [13]. Although spark durations may readily be varied by introducing resistive or inductive loads, these components absorb stored capacitor energy and it is the energy dissipated in the spark gap that is important. The product of voltage (V) and current (I) across the spark gap may be integrated with time to give dissipated energy, and this is facilitated by using rectangular V•I pulses such as in [14] and avoidance of oscillatory waveforms.

Table C.3: Lowest Reported Minimum Ignition Energies (Optimum Concentrations), Stoichiometric Concentrations and Flammable Limits (vol %) of Gases and Vapors

Gas (in air @ STP except as noted)	LMIE (mJ)	Stoichiometric (%)	Limits (%)
acetaldehyde	0.37	7.73	4.0 - 57.0
acetone	1.15 @ 4.5%	4.97	2.6 - 12.8
acetylene	0.017 @ 8.5%	7.72	2.5 - 100
acetylene (in oxygen)	0.0002 @ 40%		
acetylene (decomposition @ 1 atm)	10^3-10^5	100	100
acetylene (decomposition @ 2 atm)	100-1000	100	100
acrolein	0.13	5.64	2.8 - 31
acrylonitrile	0.16 @ 9.0%	5.29	3.0 - 17.0
allyl chloride	0.77		2.9 - 11.1
ammonia	680	21.8	15 - 28
benzene	0.2 @ 4.7%	2.72	1.3 - 8.0
1,3-butadiene	0.13 @ 5.2%	3.67	2.0 - 12
butane	0.25 @ 4.7%	3.12	1.6 - 8.4
n-butyl chloride	1.24	3.37	1.8 - 10.1
carbon disulfide	0.009 @ 7.8%	6.53	1.0 - 50.0
cyclohexane	0.22 @ 3.8	2.27	1.3 - 7.8
cyclopentadiene	0.67		
cyclopentane	0.54	2.71	1.5 -
cyclopropane	0.17 @ 6.3%	4.44	2.4 - 10.4
dichlorosilane	0.015	17.36	4.7 - 96
diethyl ether	0.19 @ 5.1%	3.37	1.85 - 36.5
diethyl ether (in oxygen)	0.0012		2.0 - 82
diethyl ether (in nitrous oxide)	0.0012 @ 14%		
dihydropyran	0.36		
diisobutylene	0.96		1.1 - 6.0
diisopropyl ether	1.14		1.4 - 7.9
dimethoxymethane (methylal)	0.42		2.2 - 13.8
2,2-dimethylbutane	0.25 @ 3.4%	2.16	1.2 - 7.0
dimethyl ether	0.29		3.4 - 27.0
2,2-dimethyl propane	1.57		1.4 - 7.5
dimethyl sulfide	0.48		2.2 - 19.7
di-t-butyl peroxide	0.41		
ethane	0.24 @ 6.5%	5.64	3.0 - 12.5
ethane (in oxygen)	0.0019		3.0 - 66
ethyl acetate	0.46 @ 5.2%	4.02	2.0 - 11.5
ethylamine	2.4	5.28	3.5 - 14.0
ethylene	0.07		2.7 - 36.0
ethylene (in oxygen)	0.0009		3.0 - 80
ethyleneimine	0.48		3.6 - 46
ethylene oxide	0.065 @ 10.8%	7.72	3.0 - 100
ethylene oxide (decomposition : no oxidant)	~ 1500	100	100
furan	0.22	4.44	2.3 - 14.3
heptane	0.24 @ 3.4%	1.87	1.05 - 6.7
hexane	0.24 @ 3.8%	2.16	1.1 - 7.5
hydrogen	0.016 @ 28%	29.5	4.0 - 75
hydrogen (in oxygen)	0.0012		4.0 - 94
hydrogen (in nitric oxide)	8.7		
hydrogen sulfide	0.068		4.0 - 44
isooctane	1.35		0.95 - 6.0
isopentane	0.21 @ 3.8%		1.4 - 7.6
isopropyl alcohol	0.65	4.44	2.0 - 12.7
isopropyl chloride	1.08		2.8 - 10.7
isopropylamine	2.0		

methane	0.21 @ 8.5%	9.47	5.0 - 15.0
methane (in oxygen)	0.0027		5.1 - 61
methane (in nitric oxide)	8.7		
methanol	0.14 @ 14.7%	12.24	6.0 - 36.0
methylacetylene (propyne)	0.11 @ 6.5%		1.7 -
methylene chloride (dichloromethane)	> 1000		14 - 22
methyl ethyl ketone (2-butanone)	0.53 @ 5.3%	3.66	2.0 - 12.0
methyl butane (isopentane)	0.25		1.4 - 7.6
methyl cyclohexane	0.27 @ 3.5%		1.2 - 6.7
methyl formate	0.4		4.5 - 23
n-pentane	0.28 @ 3.3%	2.55	1.5 - 7.8
2-pentene	0.18 @ 4.4%		
propane	0.25 @ 5.2%	4.02	2.1 - 9.5
propane (in oxygen)	0.0021		
propionaldehyde (propanal)	0.32		2.6 - 17
n-propyl chloride	1.08		2.6 - 11.1
propylene	0.28		2.0 - 11.0
propylene oxide	0.13 @ 7.5%		2.3 - 36.0
isopropyl mercaptan	0.53		
tetrahydrofuran	0.54		2.0 - 11.8
tetrahydropyran	0.22 @ 4.7%		
thiophene	0.39		
toluene	0.24 @ 4.1%	2.27	1.27 - 7.0
trichlorosilane	0.017		7.0 - 83
triethylamine	0.75	2.10	
2,2,3-trimethyl butane	1.0		
vinyl acetate	0.7	4.45	2.6 - 13.4
vinyl acetylene	0.082		1.7 - 100
xylene	0.2	1.96	1.0 - 7.0

Sources for Table C.1

[a] Haase, H., "Electrostatic Hazards : Their Evaluation and Control", Verlag Chemie, Weinheim, New York, (1977).

[b] Britton, L.G., and Smith, J.A., "Static Hazards of Drum Filling, Part I : Actual Incidents and Guidelines", Plant/Operations Progress, Vol. 7, No. 1 (January 1988).

[c] Berufsgenossenschaft der Chemischen Industrie, Statische Elektrizitat, Richt. Nr. 4, Aug 4 (1980).

[d] NFPA 325M "Fire Hazard Properties of Flammable Liquids, Gases and Volatile Solids", National Fire Protection Association, Quincy MA (1984).

[e] Lewis, B., and von Elbe, G., "Combustion, Flames and Explosions of Gases", 2 nd Ed., Academic Press, NY (1961).

[f] HERC Data Guides, Hazards Evaluation & Risk Control Services, Hercules Incorporated, Rocket Center WV.

[g] Ivanov, B.A., and Kogarno, S.M., "Explosive Properties of Pure Acetylene and its Mixtures with Other Gases", Int. Chem. Engineering, Vol. 4, No. 4, October (1964).

Notes: Reference [d] was the preferred source for flammable limit data. Reference [c] was the preferred source for MIE data where these conflicted with [a or f]. Stoichiometric compositions were taken mainly from [f].

Minimum Ignition Energies of Mists

Mists of combustible liquids can ignite and burn at less than the flash-points of the liquids concerned (even below the freezing points of the liquids). Special techniques have been used for producing mists of well-characterized size distribution and for MIE testing of both quiescent [16] and flowing [15,18] mist-air mixtures. The MIE of quiescent mist has been found to vary with the cube of Sauter Mean Diameter of the suspension and the absolute values correspond well with those predicted by theoretical models [16,18].

The Sauter Mean Diameter "D" is the diameter of a droplet whose volume-to-surface ratio is equal to that of the mist as a whole. It is defined by the size distribution statistical parameter $D_{3,2}$, which is numerically equal to the harmonic mean of the weight distribution, and lies between the means of the number and weight distributions:

$$D_{3,2} = \Sigma \{n_i d_i^3 / (n_i d_i^2)\}$$

where n_i = number of particles of diameter d_i

Depending on volatility the MIE of a mist approaches that of the vapor at a sufficiently small D, which is typically a few tens of microns [16,18]. Under these conditions the mist is rapidly evaporated by the spark and during propagation will evaporated ahead of the flame front. The hazard of fine mists is related not only to ignition energy (which varies with the cube of D) but also to burning velocity, which for a range of D might exceed that of the vapor at the same fuel-air ratio [19]. As D is decreased, the burning velocity first increases to a maximum then decreases again to approach that of the premixed gas mixture. Combustion around a droplet occurs predominately at the optimum composition (that is, near stoichiometric) some distance from the droplet surface, while expansion of gas between the burning droplets intensifies the transport process and accelerates burning. A premixed gas mixture is restrained to burn at its overall stoichiometry, which might be far from optimum.

Model for Mist Ignition Energy

The model is based on the "Simple Chemically Reacting System" or SCRS described by Spalding [20], which defines a dimensionless "mass transfer driving force" B to represent the ratio of (excess enthalpy in the bulk of the gas adjacent to the droplet surface) to the (enthalpy increase of the liquid vaporizing). Ballal [16] used the SCRS approach to derive predictions of the effect of B and droplet diameter on the ignition energy of liquid mists. Experiments were performed to test the model using a series of fuel mists. The expression for MIE was [16]:

$$MIE = \{(\pi / 6) \cdot c_{p,a} \cdot \Delta T_{st} \cdot D^3 / \rho_a^{0.5}\} \cdot \{\rho_f / [(\phi \ln (1+B))]\}^{3/2} \qquad (C.1)$$

where
- $c_{p,a}$ = specific heat of air at constant pressure
- ΔT_{st} = temperature rise for stoichiometric combustion
- D = mean particle diameter ($D_{3,2}$)
- ρ_a = air density
- ρ_f = fuel density
- ϕ = equivalence ratio
- B = mass transfer number

The mass transfer number B represents the ratio of the (energy available for vaporization) to the (energy required for vaporization) and may be thought of as a driving force for mass transfer. It can be expressed as:

$$B = c_{p,a} (T_{st} - T_{bp}) / \Delta H \qquad (C.2)$$

As discussed above, the stoichiometric flame temperature (T_{st}) is used because combustion around the droplets naturally predominates at a distance where the optimum mixture is present. The selection of the droplet surface temperature T_{bp} is discussed below. The enthalpy change for vaporization is given by:

$$\Delta H = L_v + c_{p,f} (T_{st} - T_f) \qquad (C.3)$$

where L_v = heat of vaporization
T_f = initial fuel temperature

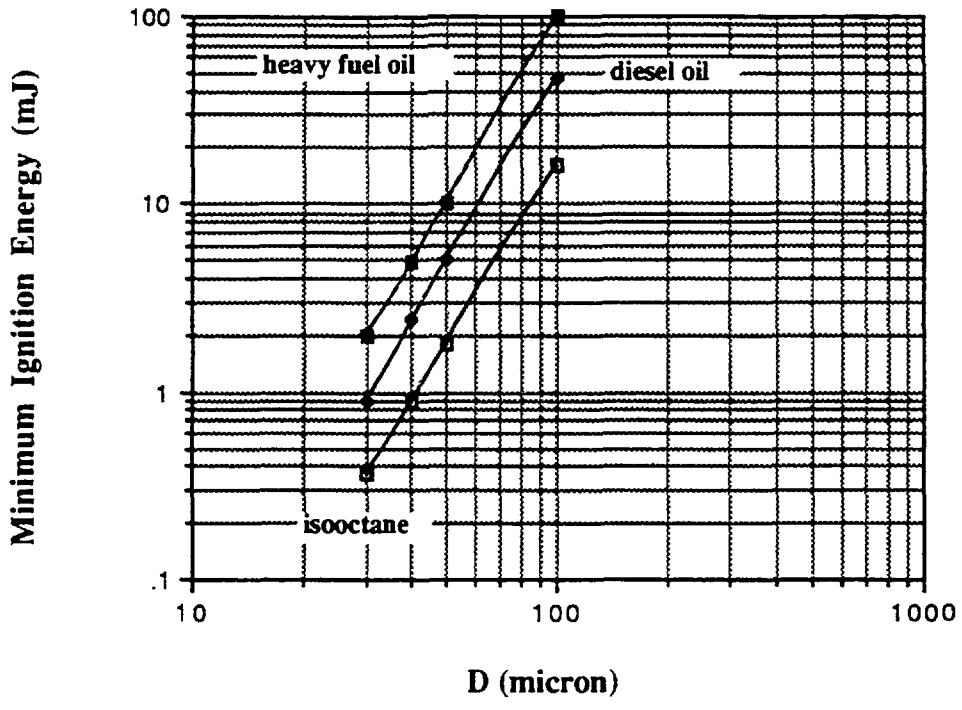
The dimensionless parameter B increases with "volatility" and typically lies between 1.2 and about 8 as shown in Table C.2 [16]:

Table C.2 : Mass Transfer Numbers of Liquid Fuels

liquid		B
heavy fuel oil	=	1.5
light fuel oil	=	2.5
diesel oil	=	2.8
gas oil	=	3.1
kerosene	=	3.7
isooctane	=	6.1

A problem with the overall approach for liquid mixtures is that suitable averages must be calculated for B and for the air properties at the average gas temperature. However, the error is offset by the logarithmic term in C.1. Peters [18] used the arithmetic mean of the ambient air and stoichiometric flame temperatures (that is, at 1300 K) to evaluate $c_{p,a}$ and ρ_a. Since ignition limits of fuel mixtures correlate well with the 10% evaporation point, this was taken as the fuel boiling point in evaluation of the droplet surface temperature (needed to calculate B). Figure C.1 adapted from [16] shows experimentally-verified ignition energies for three of the above fuels as a function of D, all at an equivalence ratio of 0.65. From this the important effect of diameter is apparent.

Figure C.1 : Effect of Droplet Diameter D on MIE of Mist



APPENDIX D : LIMITING OXYGEN CONCENTRATIONS

The Limiting Oxygen Concentration is a special case of Limiting Oxidant Concentration (LOC) where oxygen is the oxidant. The LOC is the minimum concentration of oxidant needed to support a deflagration where the gas is initially at atmospheric temperature and pressure. Most available data are for oxygen as oxidant. No data have been found in the literature for oxidants such as chlorine. Since the most common oxidant is air, most data have been developed for mixtures of flammable materials in air to which an inert diluent such as carbon dioxide or nitrogen has been added to reduce the oxygen concentration. The LOC depends on the diluent used to reduce the oxygen concentration.

Although the ignition energy is increased with oxidant concentration reduction, this effect is not known quantitatively. Partial inertion to render a vapor space immune to weak ignition sources such as static can not therefore be supported.

Materials capable of propagating a decomposition flame at or near to atmospheric pressure are assigned a LOC of zero. Where elevated pressures are required the minimum propagation pressure at about 25 C given in Bureau of Mines Bulletin 680 is shown.

The LOC is reduced as temperature and pressure are increased, and for processes operating at elevated temperature and/or pressure this effect must be considered. Also, the LOC depends on the strength of the ignition source. In order to safely apply LOCs for process inerting, it is necessary to allow for additive errors in test data and field implementation as discussed in the text. Klinkenberg [1] states that mixtures of hydrocarbon vapor, air and inert gas containing less than 10 vol% of oxygen cannot be ignited. This is not always true (for example, styrene or diethylbenzene with nitrogen diluent). Table D.1 is otherwise exerpted from NFPA 69.

Table D.1 : Limiting Oxygen Concentrations

Gas or Vapor	LOC (Air + N_2 Diluent)	LOC (Air + CO_2 Diluent)
acetaldehyde	n/a	n/a
acetone	11.5	14
acetylene	ZERO	ZERO
acrolein	n/a	n/a
benzene	11.4	14
butadiene	10.5	13
t-butanol	n/a	16.5 (100°C)
iso-butane	12	14.5
n-butane	12	14.5
1-butene	11.5	14
n-butyl chloride	14	n/a
n-butyl chloride	12 (100°C)	n/a
isobutylene	12	15
isobutyl formate	12.5	15
carbon disulfide	5	7.5
carbon monoxide	5.5	5.5
chloroazide	ZERO	ZERO
cyclopropane	11.5	14
diethylbenzene	8.5	n/a
dimethyl hydrazine (UDMH)	7	n/a
divinylbenzene	8.5	n/a
ethane	11	13.5
ethanol	10.5	13
ethyl benzene	9.0	n/a

2-ethyl butanol	9.5 (150°C)	n/a
ethylene (1 atm)	10	11.5
ethylene (>4650 cmHg)	ZERO	ZERO
ethylene dichloride	13	n/a
ethylene dichloride	11.5 (100°C)	n/a
ethylene oxide	ZERO	ZERO
ethyl ether	10.5	13
ethyl nitrate	ZERO	ZERO
gasoline (73/100)	12	15
gasoline (100/130)	12	15
gasoline (115/145)	12	14.5
germane*	ZERO	ZERO
n-heptane	11.5	14.5
n-hexane	12	14.5
hydrazine	ZERO	ZERO
hydrogen	5	5.2
hydrogen sulfide	7.5	11.5
JP-1 fuel	10.5 (150°C)	13 (150°C)
JP-3 fuel	12	14.5
JP-4 fuel	11.5	14.5
kerosene	10 (150°C)	13 (150°C)
methane	12	14.5
methanol	10	12
methyl acetate	11	13.5
methyl acetylene (1 atm)	n/a	n/a
methyl acetylene (>300 cmHg)	ZERO	ZERO
3-methyl-1-butene	11.5	14
methyl chloroform	14	n/a
methylene chloride	19 (30°C)	n/a
methylene chloride	17 (100°C)	n/a
methyl ether	10.5	13
methyl ethyl ketone	11	13.5
methyl formate	10	12.5
monochloroacetylene	ZERO	ZERO
natural gas (Pittsburgh)	12	14.5
iso-pentane	12	14.5
n-pentane	12	14.5
propadiene (1 atm)	n/a	n/a
propadiene (>169 cmHg)	ZERO	ZERO
propane	11.5	14.5
propargyl bromide	ZERO	ZERO
propargyl chloride	ZERO	ZERO
propylene	11.5	14
propylene oxide	7.8	n/a
silane*	<1	<1
styrene	9.0	n/a
toluene	9.5	n/a
trichloroethylene	9 (100°C)	n/a
vinyl chloride	13.4	
vinylidene chloride	15	
vinyltoluene	9.0	n/a

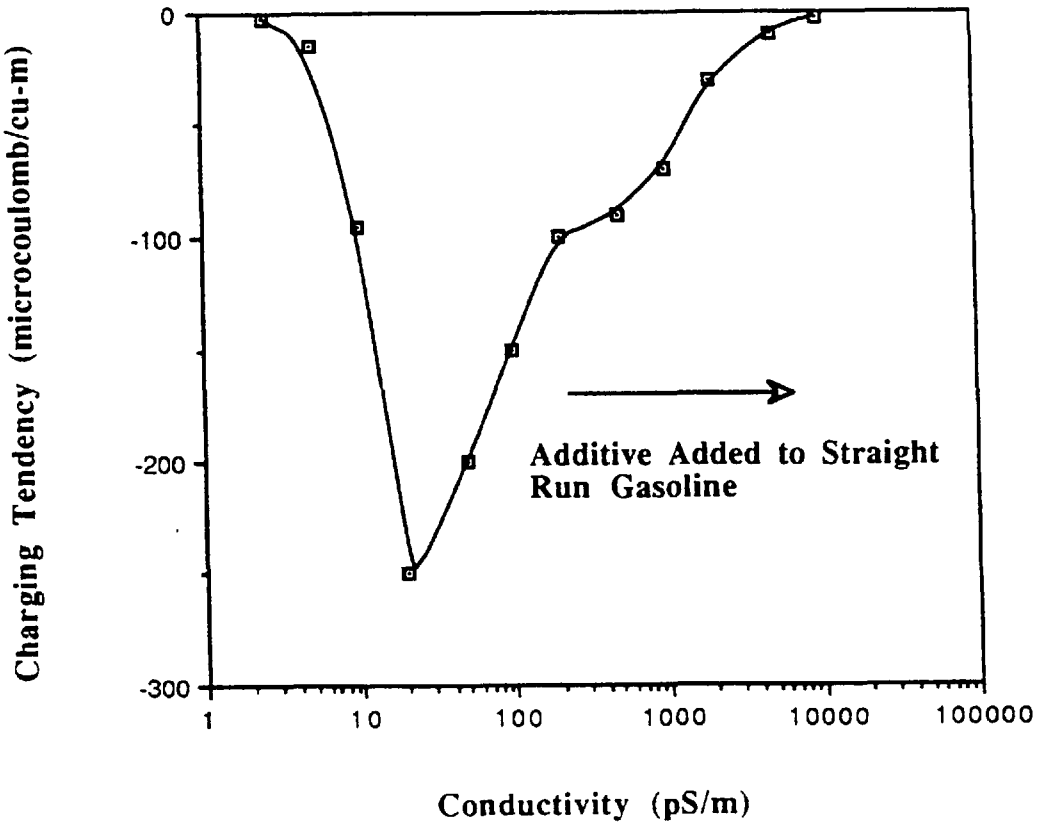
APPENDIX E : STATIC GENERATION AND RELAXATION IN PIPES AND HOSES

When a low conductivity liquid is pumped through a pipe, it is found that the charge density achieves a steady-state value after a certain pipe length. The steady-state is achieved once the rate of charge generation at the wall equals the rate of relaxation back to it.

Effect of Liquid Conductivity on Charging in Pipes

During flow through pipes, it has been found that the charge density passes through a maximum value which depends upon the liquid plus any contaminants present, and the flow conditions. The maximum is usually about two orders of magnitude greater than the minima, which respectively occur at low conductivity (below about 1 pS/m) and high conductivity (above about 10000 pS/m). Figure E.1 shows test data adapted from Klinkenberg [1] and the relative magnitudes are in agreement with data presented by Lloyd [23]. While the charge generation rate increases with conductivity, so does relaxation rate and eventually the latter effect dominates. It should be noted that charge densities in pipe flow remain relatively large up to at least 1000 pS/m. Thus in non-conductive receiving tanks large liquid surface potentials may be generated, and "safe" conductivities of (typically) 50 pS/m based on relaxation in grounded metal tanks do not apply.

Figure E.1 : Effect of Conductivity on Charging in Pipes



Empirical Charging Models

Charge generation in flowing liquids is described in terms of double-layer theory. Assuming the presence of ions in a liquid, adsorption of ions at the wall will not be uniform, and so there will exist a fixed layer of ions at the wall having a certain net polarity. Further from the wall, a diffuse layer of ions with net countercharge will exist. This layer can be sheared during flow and convected downstream as a "streaming current". The theory is well developed for conductive systems of defined electrolytes. In systems containing low-conductivity liquids, only the modulus of the streaming current can usually be estimated by reference to empirical data. Double layer theory has met with limited success. Even with empirical methods, it is found that polarity can change in a given system.

Empirical methods are described in [3]. The best known equation is that due to Schon [22], who found that the steady-state charge density for turbulent gasoline flow in long, smooth wall pipes is proportional to velocity:

$$S = \beta v \qquad (C/m^3) \qquad (E.1)$$

where
- S = final steady-state charge density emerging from pipe
- β = proportionality constant (4.77×10^{-6} C.s.m.$^{-4}$)
- v = flow velocity (m.s.$^{-1}$)

Equation E.1 can be written in terms of the streaming current flowing out of a long pipe, since this is simply the product of charge density, velocity and cross-sectional area of the pipe:

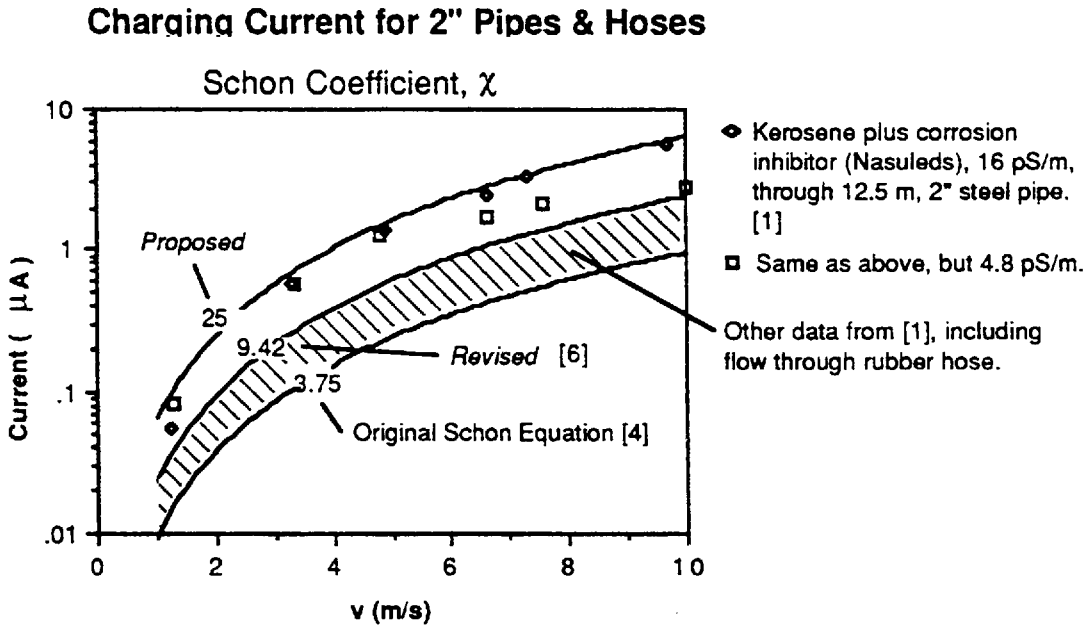
$$I_S = \chi v^2 d^2 \qquad (E.2)$$

where
- I_S = streaming current (A)
- χ = proportionality constant (3.75×10^{-6} C.s.m.$^{-4}$)
- d = pipe diameter (m)

In the original Schon study [22], gasoline with conductivity in the range 0.01 - 10 pS/m flowed through 20 m long pipes having diameters in the range 2.5 - 20 cm. The value of the exponent in E.2 varied from 1.8 - 2.0. Equation E.2 has been simplified by the adoption of a conservative exponent of 2.0.

Subsequent work by Strawson, reviewed in [4], suggested that this equation is not conservative in all cases, and revised values of 1.2×10^{-5} and 9.42×10^{-6} (Csm^{-4}) were recommended for the constants β and χ respectively. Later evaluation by Britton [7] of Klinkenberg data [1] in which a corrosion inhibitor (Nasuleds) was present showed that even higher values of β and χ were necessary to envelope these data. β and χ were increased to 31.8 x 10^{-6} and 25 x 10^{-6} respectively. Figure E.2 shows three versions of equation E.2 using the three different values of χ, plus the Klinkenberg data from [1].

Figure E.2



As shown in Figure E.2, while most of the data given in [1] fall below the predicted levels using the revised Schon equation [4,7], including data for smooth-bore rubber hoses, higher streaming currents were found when "Nasuleds" corrosion inhibitor was added to the kerosene. This additive acted as a pro-static agent. It can be seen that streaming currents greater than 1 microampere may be generated at about 4 m/s with the pro-static agent present, whereas other data indicate that about 7 m/s would be required to generate this current.

Application to Pipes of Finite Length

The Schon equation should apply to smooth-bore pipes in which the liquid residence time is very long compared to its relaxation time (or time constant). For pipes not meeting this criterion, the effluent charge density should gradually increase to its steady-state (infinite pipe length) value. Liquids can be assumed to lose charge exponentially in grounded systems according to:

$$S = S_0 e^{-t/\tau} \qquad \text{(E.3)}$$

where S_0 = initial charge density (C/m^3)
t = elapsed time (s)
τ = time constant (s)

For liquid flow in pipes of different lengths, the variation of effluent charge density with residence time can be shown theoretically to follow the relationship [1, p. 60]:

$$S = S_\infty (1 - e^{-t/\tau}) \qquad (C/m^3) \qquad \text{(E.4)}$$

where S_∞ = steady-state charge density (infinitely long pipe)

The effluent charge density S approaches its steady-state value when **t** becomes large compared with time constant τ. Both **t** and τ can be written in terms of measured quantities. The time of flow for any liquid element is given by the pipe length divided by flow velocity. The time constant can be written in terms of liquid conductivity and dielectric constant:

$$\tau = \varepsilon_o \varepsilon_r / \sigma \qquad \text{(E.5)}$$

where

e_o = permittivity of vacuum = 8.854×10^{-12} (F/m)
e_r = dielectric constant of liquid
σ = liquid conductivity (S/m)

Values of ε_r and σ are given in Appendix B for a series of flammable liquids. Note that for non-conductivity liquids (σ less than a nominal 50 pS/m) the conductivity is sample-dependent. Low conductivity liquids include ethers, aliphatic, aromatic and cyclic hydrocarbons, carbon disulphide and some silicon-based liquids. They usually, but not exclusively, have dielectric constants of less than 4. Conductive materials include alcohols, aldehydes, ketones, acids, epoxides, esters and nitriles. For materials not specifically mentioned, conductivity should be ascertained according to the Standard Test Method ANSI/ASTM D 3114-72.

If the Schon Equation is formulated in terms of the most conservative values of proportionality constants β and χ as suggested above, one obtains the final forms:

$$S = 3.18 \times 10^{-5} \, v \, (1 - e^{(-\kappa L)/(\varepsilon_o \varepsilon_r v)}) \quad (C/m^3) \qquad \text{(E.6)}$$

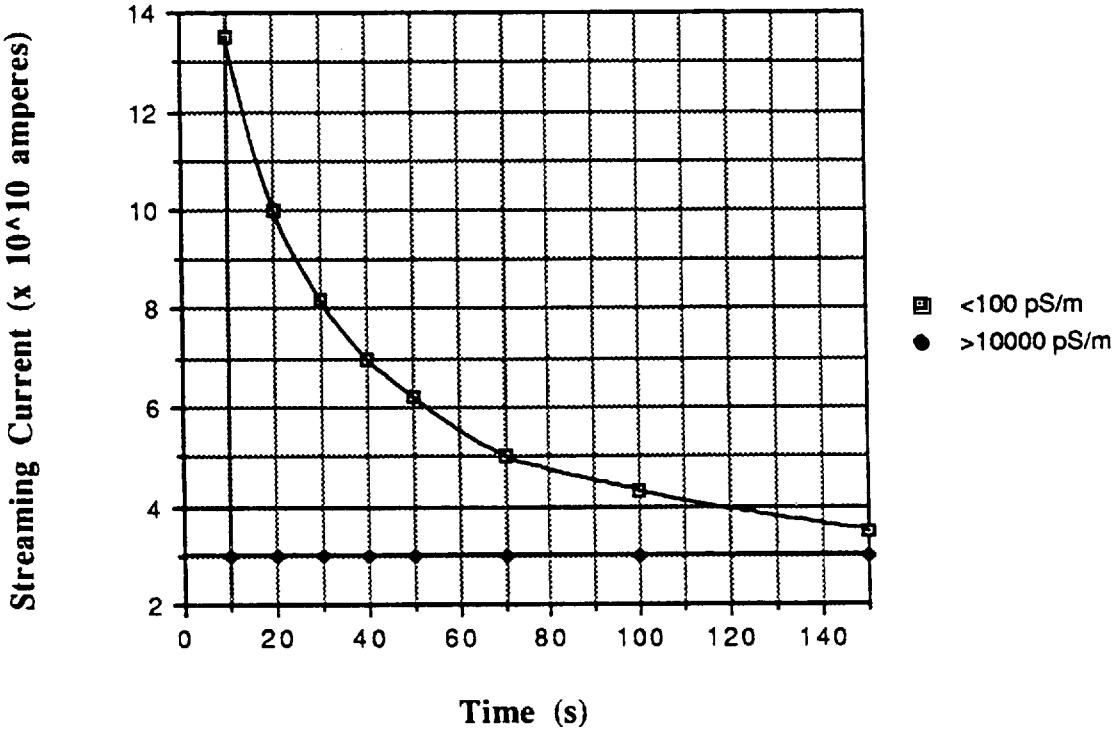
$$I_S = 2.5 \times 10^{-5} \, v^2 \, d^2 \, (1 - e^{(-s L)/(\varepsilon_o \varepsilon_r v)}) \quad (A) \qquad \text{(E.7)}$$

These equations envelope published data for charge generation in smooth metal pipes and rubber hoses (moderate resistivity) with large lengths. The application to shorter pipes and hoses (where the exponential expression in E.6 and E.7 are significantly greater than zero) is approximate, given the practical non-idealities of the relaxation process.

Plastic Pipes of Very High Resistivity

Lloyd [23] states that with liquids of low conductivity (1 - 100 pS/m), the component of charge that is absorbed on plastic pipe walls cannot migrate quickly along it and its presence tends to impede further charge separation. As a result the streaming current decreases with time as shown in Figure E.3. Conductive liquids (>10^4 pS/m) form a conductive layer on the pipe wall creating a leakage path and preventing charge accumulation. The streaming current remains constant with time of flow in the same manner as a metal pipe.

Figure E.3 : Charging in High Resistivity Pipe



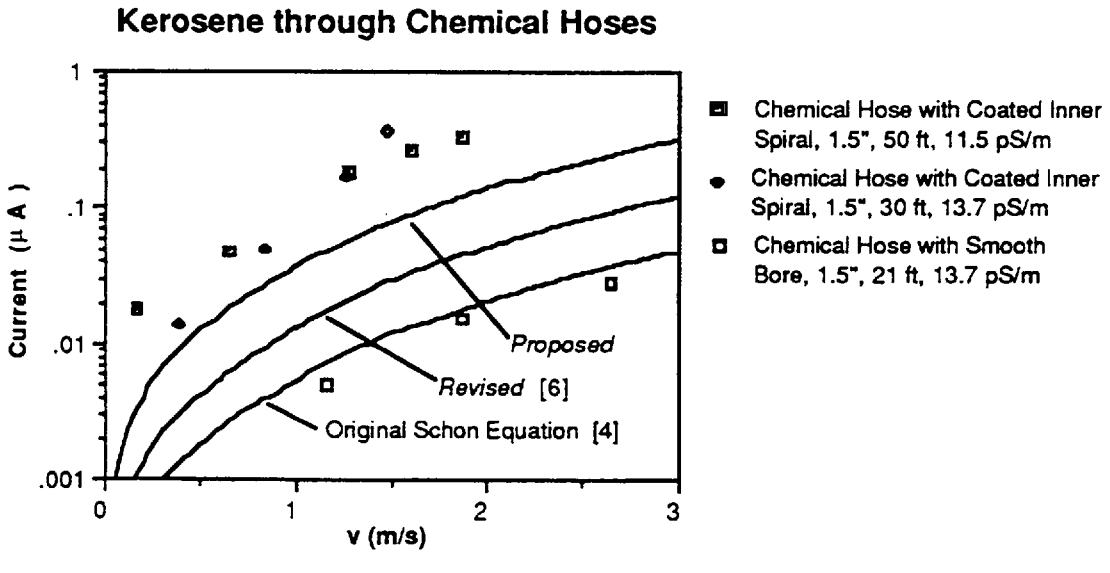
Chemical Hoses : Smooth versus Rough Bore

Hoses containing inner spirals introduce a "roughness factor" which serves to increase turbulence and the effluent charge density can be increased significantly, at least in hoses with diameter of about 2 inches or less (see Table E.1). This table shows that hazardous charge densities were produced with the spiral wound hoses even at flow velocities less than 2 m/s. In the chemical industry, it is not unusual to load liquids such as toluene through such small diameter hoses. Figure E.4 shows a scattergram of streaming currents for smooth and rough bore hoses compared with the empirical "smooth pipe" predictions of the three "Schon" equations given in Figure E.2.

Table E.1 : Charging in 1.5 Inch Inside Diameter Chemical Hoses using Kerosene of Conductivity 11.5-13.7 pS/m [7]

Hose	Flow Rate (gpm)	Velocity (m/s)	I_S (nA)	S_o ($\mu C.m^{-3}$)
50 ft. (new) Chemiflex TIFT (coated inner spiral)	7	0.39	14	32
	15	0.83	50	53
	21	1.16	170	128
	27	1.49	370	217
30 ft. (used) Chemiflex TIFT (coated inner spiral)	3	0.17	18	95
	11	0.63	47	68
	23	1.26	190	131
	29	1.59	270	148
	34	1.88	330	154
21 ft. MGT Coronado smooth bore hose	21	1.16	5	4
	34	1.88	15	7
	48	2.65	28	9

Figure E.4 : Effect of Internal Spiral on Charging in Two-Inch Hose



The theoretical aspects of charging at restrictions in pipes were discussed by Goodfellow et al. [30].

Charge Relaxation in Plastic Pipes

Lyle and Davies [42] studied five types of plastic pipe including PTFE, and showed that the rate of charge relaxation from flowing kerosene was the same for a steel pipe of equal dimensions. From both experiment and theory it was suggested that the charge moves to the inside

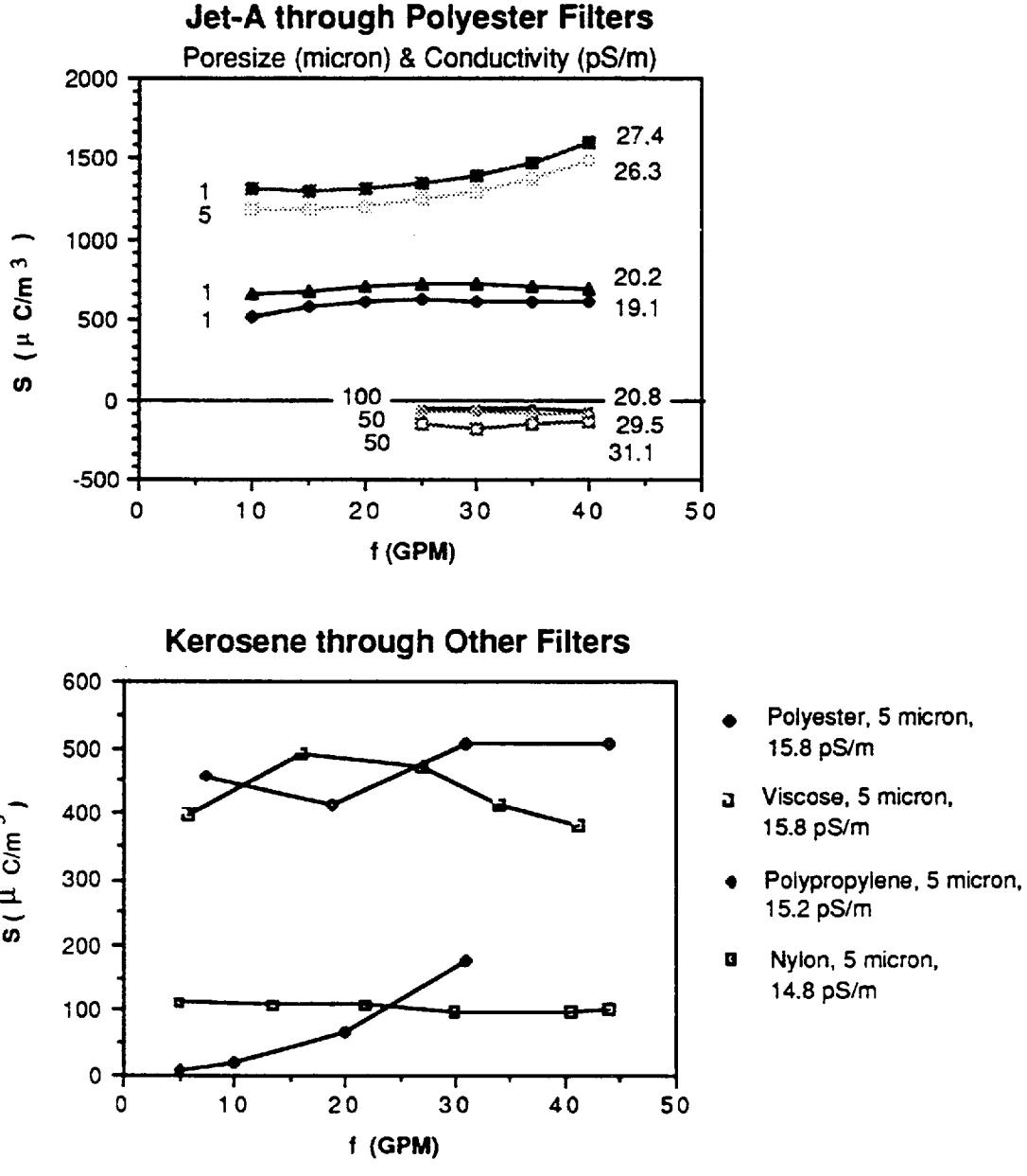
surface of the pipe, and if both the inlet charge density and the pipe material viscosity are high enough, the charge accumulates until spark discharges are produced. In such cases the spark discharges can take place through the pipe wall and can cause puncturing and leakage of liquid.

These findings are not unique and have been confirmed elsewhere.

APPENDIX F : CHARGING IN SCREENS AND MICROFILTERS

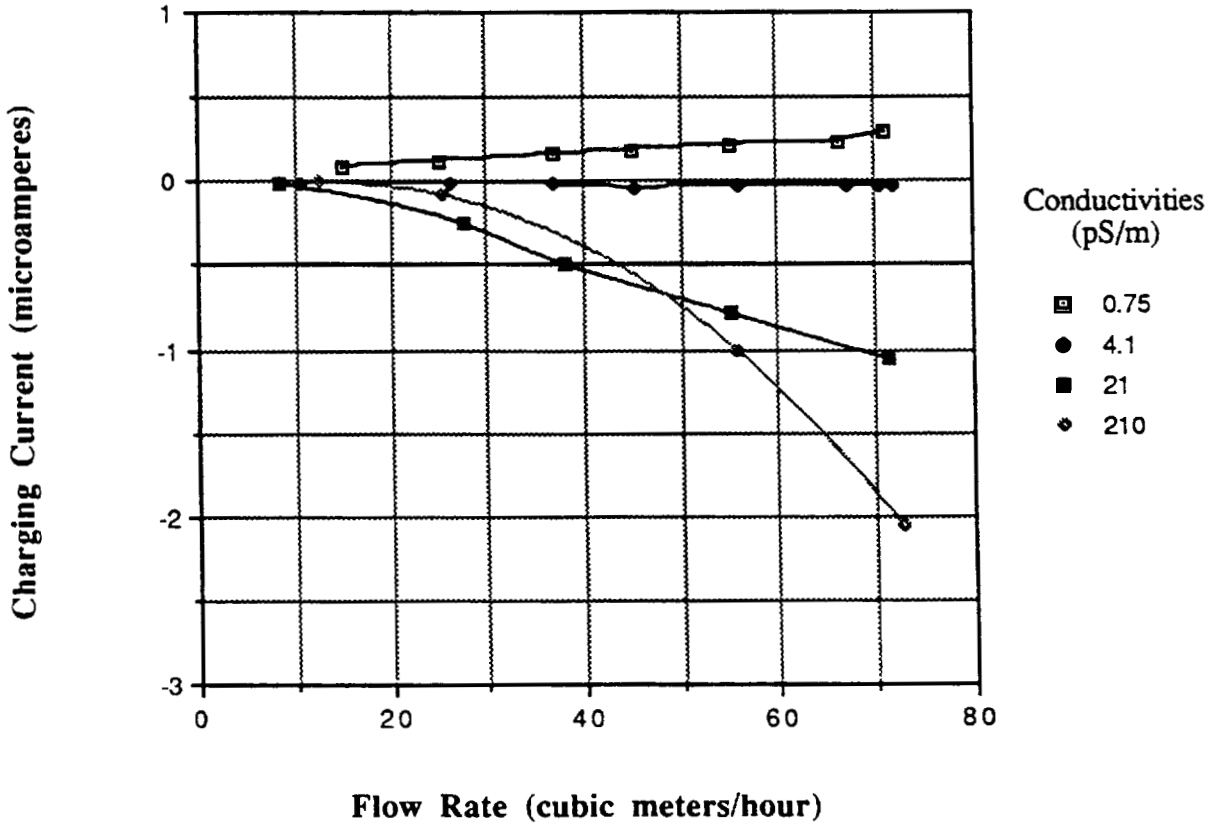
Owing to its large contact surface area, the most significant static generator in filling systems is the in-line filter. After liquid passes through the filter its charge density increases transiently to a value 1-3 orders of magnitude higher than the steady-state "smooth pipe" value. Figure F.1 shows the charge densities produced from polyester bag filters of various nominal pore sizes in a 2 inch line at different flow rates and liquid conductivities. It is seen that the charge density is roughly independent of flow rate and velocity, but since charging current is proportional to flow rate one would expect a proportionality between these.

Figure F.1 : Charging of Kerosene in Bag Filters in Two-Inch Line



Data presented by Klinkenberg [1] for charging current of Cr-Ac doped kerosene flowing through an impregnated paper filter is adapted in the Figure F.2. This suggests that the charging current was roughly independent of flow rate in this system at low conductivity values. Similar data were presented in [1] for corrosion inhibitor doped kerosene flowing through a paper filter of different design.

Figure F.2 : Effect of Conductivity on Charging Current from Paper Filters



Theories for Microfilter Charging

APPENDIX G : DISCHARGES

Sparks

Spark breakdown in air between flat electrodes (uniform electric field) occurs at an electric field of 3 MV/m and at rather higher fields at an electrode having a small radius of curvature. Table G.1 [38] gives some calculated values for sphere-plane geometry. These were obtained by experimentally determining the electrode radii and gaps at which breakdown occurred to a large metal sheet held at fixed potential, then calculating the respective fields at the electrode using a mathematical model.

Table G.1 : Calculated Breakdown Fields at Grounded Electrode

Radius of Curvature (mm)	Breakdown Field (MV/m)
3.5	6.3
6.4	5.3
12.7	4.6
31.5	4.0
∞	3.0

These are the breakdown fields at the spherical electrode. A further criterion [40] states that if the mean field in the gap (potential difference divided by gap length) exceeds 500 kV/m, and if the field at either electrode exceeds 3 MV/m, spark breakdown will probably occur. At mean fields below 500 kV/m only partial breakdown (corona or brush) will occur.

Response and Ignition Risk of Spark Discharges from People

Response depends on energy and source capacitance of the spark, in addition to personal characteristics including skin resistance and sensitivity. Female subjects are observed to react at lower energy thresholds. Response is related to power density passing through the skin. Hence if one is carrying a metal key a larger energy can be dissipated without shock when the key is used to discharge the body to ground. In practical situations involving metal tools this can result in production of sparks of at least several mJ without any perception of a shock, and the sparks may not be either audible or visible.

The important result vis-a-vis ignition hazards is that imperceptible sparks may be produced at energies considerably larger than the LMIE of most flammable gas or vapor mixtures in air.

Although spark discharges from rings and wristwatches (etc) may give efficient metal-metal spark gaps, discharges from the skin will usually involve significant quenching owing to the relatively large radii of curvature of fingers and knuckles. Therefore for equal stored energy, the risk of gas ignition will be greater at larger voltages (hence larger spark gaps) and consequently at smaller capacitance. A further skin effect is its resistance, which can cause energy losses and decrease the efficiency relative to metal-metal sparks.

Body capacitance depends on the capacitance of the feet with respect to ground plus the body capacitance with respect to all other conductors in the immediate area. Body capacitance has been measured [59] at not less than 90 pF, corresponding to a person of average height standing on the tip of one rubber boot with 18 mm sole (simulating walking with lowest contact area with the floor). While a completely isolated individual (jumping off the ground) may achieve a capacitance as low as 55 pF [59] this is not a useful value for any practical analysis. A value of

about 120 pF was found for the man in standing position, although this value can reach 200 pF or more depending on the characteristics of the footwear (ground contact area, dielectric constant and sole thickness).

Corona and Brush Discharges

It is shown in Appendix H that the maximum theoretical surface charge density on a non-conductor is about 2.7 nC/cm^2 when the flux all emanates in one direction, and about 5.3 nC/cm^2 when a two dimensional charge array is isolated in free space. Above these surface charge densities the surrounding air will begin to ionize and various partial discharge types may be produced.

For plastic surfaces it has been shown [60] that the maximum charge densities produced by rubbing the surfaces with various materials, such as woolen cloth, can approach the theoretical maximum of 2.7 nC/cm^2. Note that during any practical rubbing scenario, the flux must at some stage be in one direction, such as towards the countercharge on the rubbing medium. The theoretical maximum is not attained (2.3 nC/cm^2 was the highest observed value) owing to non-idealities allowing some ionization to occur prior to measurement.

It is shown in Appendix H that the field produced at a grounded electrode approaching the charged surface decreases as the electrode radius increases. Thus, larger charge densities can be supported with larger electrodes before ionization and breakdown of the air occurs. It follows that larger discharge energies can be produced using electrodes of larger diameter.

Corona Discharges

Corona discharges are produced in strongly divergent electric fields by conductors of small radius of curvature (typically less than 2.5 - 3 mm). They occur as a succession of so-called "Trichel Pulses" but to the observer appear as a continuous "hissing" discharge with a small luminous origin at the electrode with tip pointed in the direction of the field. The luminosity and noise increase with the source current while at small currents may not be observed without special equipment. Point-plane corona discharges are described according to the polarity of the point (electrode). Hence the terms positive and negative coronas. The characteristics of coronas including current-voltage characteristics depend on polarity in addition to geometry.

Corona discharges are non-hazardous in terms of gas ignition except at high currents that would not normally be produced during liquid transfer, but which might be produced as the result of lightning activity or operation or high voltage equipment. Sloane [65] in an early study found that 300 microamperes current was needed to ignite optimum coal gas-air mixtures using metal points 3-6 mm apart. Newman and Robb [66] in a later study reduced this threshold significantly by demonstrating ignition of aviation gasoline vapor at 200 μA. Both studies noted an increased incendivity at elevated temperature. Such currents are larger than those produced during liquid handling, even downstream of a filter. While large quantities of charge can accumulate in a tank, it is not possible to produce corona discharge currents of this magnitude owing to the localization of ionization and the electrical resistance of the charged medium. Extremely sensitive gases, such as di- and trichlorosilane, carbon disulfide and hydrogen might be ignited by corona at significantly less than 100 μA but no information is available.

Coronas are used in a variety of applications to cause static neutralization by passive or active ion injection processes.

Corona Discharge Threshold Fields

The electric field in the vicinity of a charged body such as a charged sheet of plastic is greatly magnified at the surface of any grounded wire or pointed tip. If this magnified field exceeds a certain threshold a corona discharge will occur. In atmospheric air this critical field is approximately given by [72]:

$$E_c = 3.1 \cdot m \{1 + 0.0308 / r_1^{0.5}\} \times 10^6 \quad \text{(V/m)}$$

where m = surface irregularity factor (~1)
r_1 = tip or wire surface radius (m)

As the wire radius decreases the corona onset field is raised. However, this is more than compensated for by the field magnification given approximately by:

$$E_w = s \cdot r_2 / (r_1 \cdot \varepsilon_o)$$

where s = surface charge density on plastic surface ($C.m^{-2}$)

To derive this latter expression, it was assumed [73] that a wire is mounted coaxially in a hollow tube of charged material. The radii are r_1 (wire) and r_2 (charged surface). This symmetry simplifies the geometry and allows the field at the charged plastic inner surface to be written:

$$E_s = s / \varepsilon_o$$

And application of Gauss' Law gives the field at the wire:

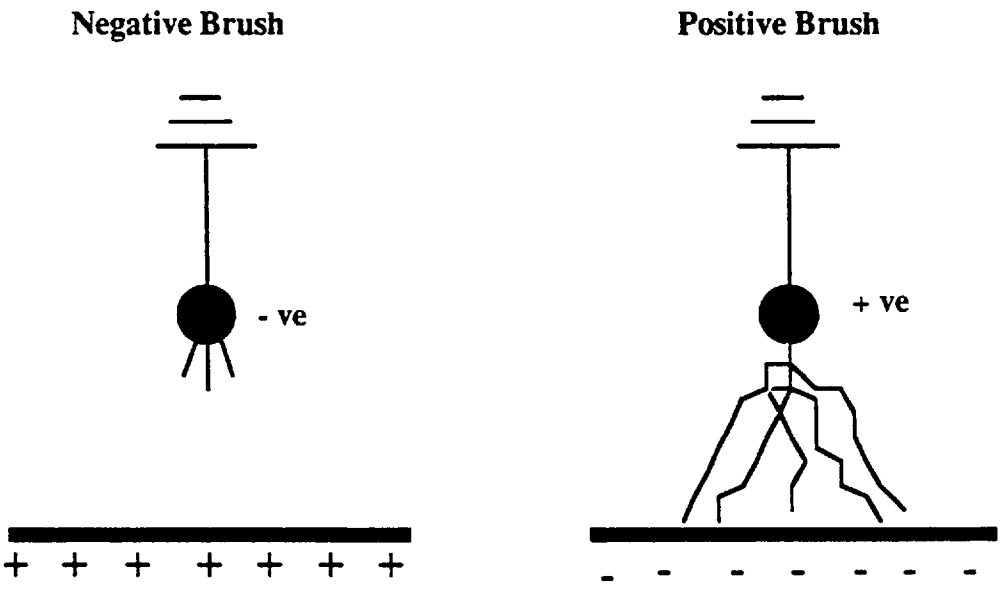
$$E_w = r_2 \cdot E / r_1$$

Effect of Polarity and Geometry on Brush Characteristics

The type of discharge produced depends on electrode diameter. For small diameters below 5 mm [61] to 7 mm [6, 38] corona discharges are typically produced. At larger diameters "brush" discharges are produced. The brush is a partial breakdown phenomenon appearing as a discrete event with numerous luminous channels emanating from the surface and joining in a bright root close to the electrode. The type of brush varies with polarity (Figure G.1) as discussed by Fredholm and Lovstrand [62], Britton and Williams [38] and Britton and Smith [6]. The phenomena occur with both charged plastics and non-conductive liquids. They are not limited to spherical electrodes and two-dimensional surfaces. They may be initiated by the approach of fingers, knuckles or metal tools to both flat and curved charged surfaces including plastic pipe and tubing.

A very impressive demonstration of ignition by brush discharges is contained in the I.Chem.E. Package 016 "Video Training Package in Controlling Electrostatic Hazards". In this video a charged plastic sheet is brought up to a gas jet on a laboratory burner and ignition is produced. The plastic sheet could represent a polyethylene drum liner which has left the drum while pouring powder into a flammable solvent. As pointed out in the video, a drum liner must NEVER be allowed to leave the drum or (especially) be shaken out in a flammable vapor atmosphere. Many industrial accidents have occurred this way. While in the drum, the liner has an adjacent conductor (metal) or semiconductor (fiber board) to form a countercharged layer and suppress the electric field. When the liner leaves the drum, a large electric field can appear, and if shaken, the field around the liner will intensify locally as the charge density is increased.

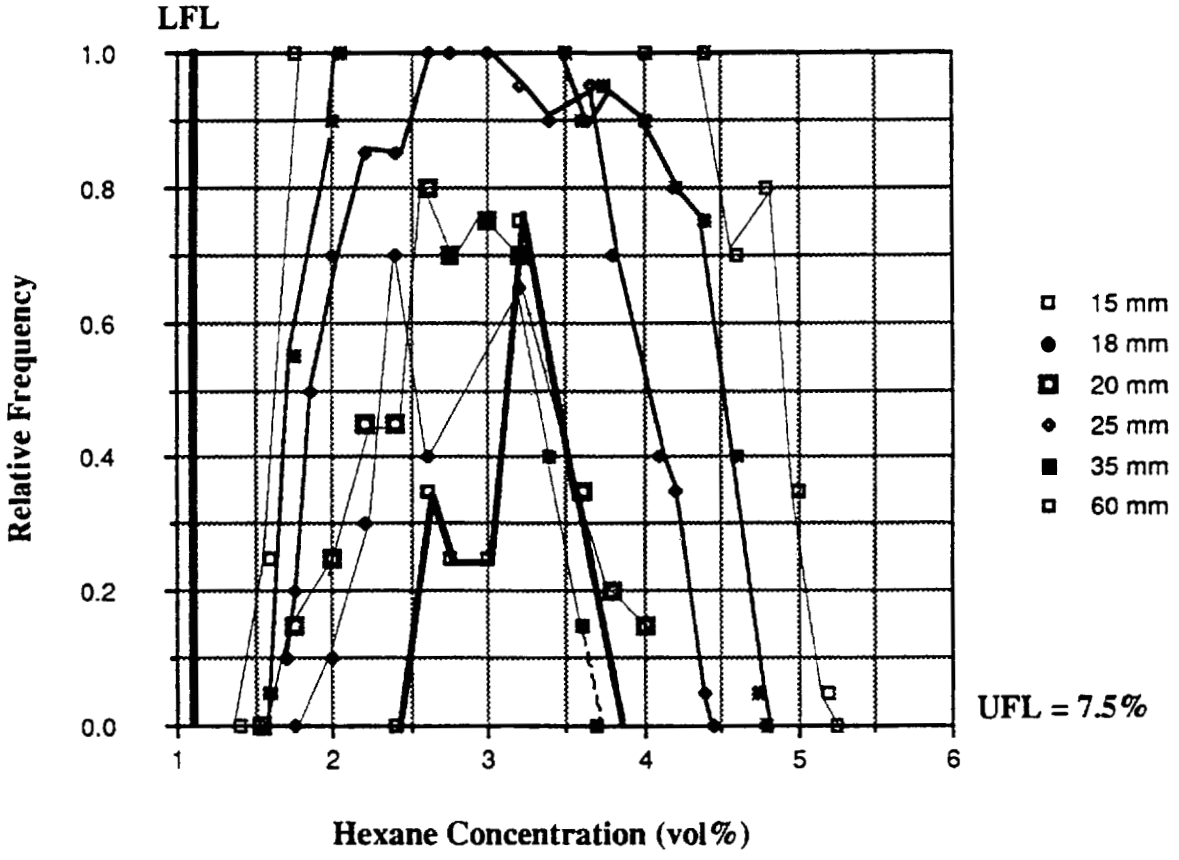
Figure G.1 : Appearance of Negative and Positive Brush Discharges



Effect of Electrode Diameter on Brush Ignition Frequency

Heidelburg [61] showed experimentally that the ignition frequency of hexane-air mixtures by brush discharges from a charged plastic surface varies with electrode diameter. The mixtures have a higher ignition frequency and can be ignited across a broader range of compositions as the electrode diameter increases, as shown in Figure G.2. The highest ignition frequency is at about 3.2% hexane. The mixture with the lowest MIE as determined by spark (Appendix C) is 3.8%. The stoichiometric mixture contains 2.16 vol% hexane. It is seen that the ignitable range at a diameter of 20 mm (the same curvature as human fingers or knuckles) is from about 1.1 to at least 4 vol%. Large electrodes of diameter 60 mm can ignite mixtures over the range 1.4 - 5.2 vol%, which comprises most of the flammable range (1.1 - 7.5 vol%).

Figure G.2 : Effect of Electrode Diameter on Brush Ignition Frequency of Hexane in Air



Maximum Effective Energy of Positive and Negative Brush Discharges

The maximum effective energy of these discharges can be found relative to capacitance sparks. Limiting cases for the highest ignition energy mixtures ignited were at 5.2 and 1.4 vol% hexane. From the data of Lewis and von Elbe [63, p. 163] these compositions have respective MIEs of about 0.7 mJ and (extrapolated) 3-4 mJ. It appears that brush discharges are less effective in igniting rich mixtures and that for lean mixtures the maximum effective ignition energy can be at least 3 mJ. Discharges from smaller electrodes (15 mm) can give effective energies up to about 0.7 mJ.

Later research published in 1981 [64] set the maximum effective energy of brush discharges from large plastic surfaces at 3.2 mJ, using test mixtures of known MIE as determined by capacitance spark.

Go-Devils

The phenomenon of "Go Devils" is described in [41] as follows. "When agitated (as in filling a tank), liquids of low conductivity will develop static sparks on the surface. The sparks dart about erratically, and may jump long distances (sparks up to 2 ft long have been observed)".

These discharges are not brush discharges but are analogous to the "wall-to-cone" (also known as "compaction" or "bulking brush") discharges observed when filling silos with powders. There has been no study of the possible effective energies of these discharges in liquid systems, but in powder systems they are believed to carry a maximum effective energy of about 10 mJ. These discharges have been described to the author by night-time observers of toluene tank truck filling. In view of the ease with which toluene forms flammable mixtures at ordinary temperatures, and the fact that such observations could be made on a non-inerted tanker, it is unlikely that such discharges normally carry effective energies greater than about 1 mJ. The observers can count themselves lucky that worst case conditions did not develop while their faces were above the manway.

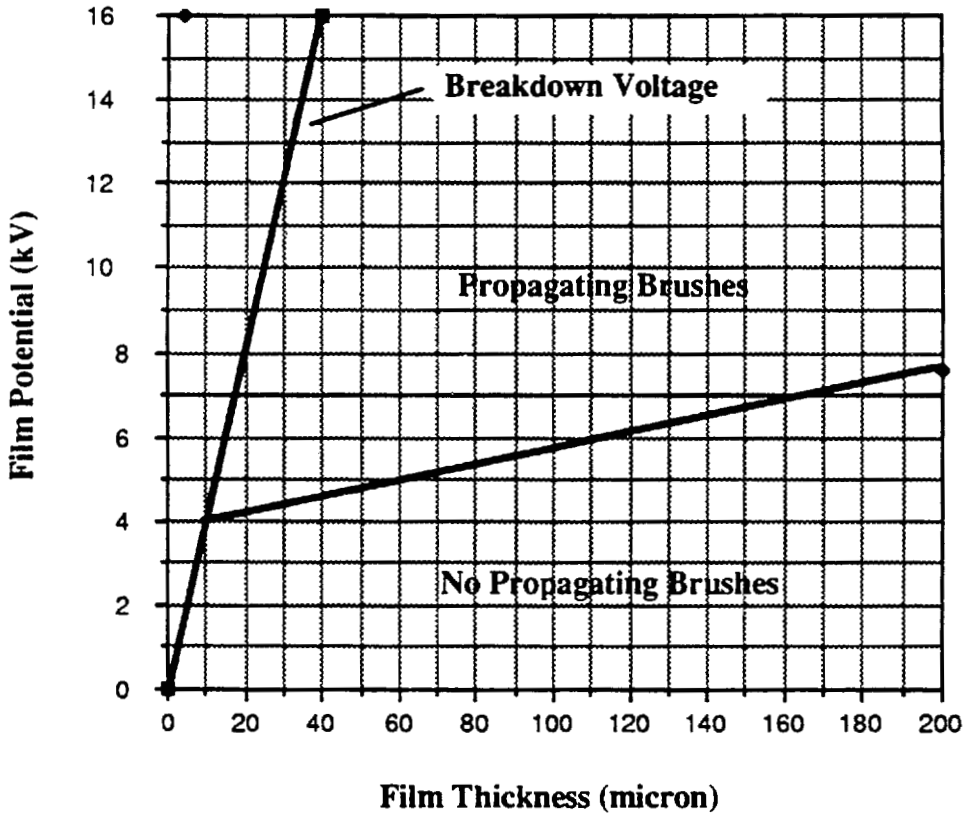
Propagating Brush Discharges

Propagating brush discharges are most readily described in terms of a parallel plate capacitor consisting of a charged, non-conductive film whose lower side is in close contact with a grounded metal plate. Provided the film is sufficiently resistive and above a certain critical thickness, as the charge density on the film is increased a regime is first reached in which brush discharges may be produced above the film and charge transfers range from less than 0.1 μC up to about 1 μC. As the charge density on the film is further increased, a transition occurs beyond which charge transfers of 20 μC up to several hundred microcoulombs are observed. These are propagating brush discharges. These discharges are typically visible and audible events and can carry energies of several Joules.

Glor [74] studied the conditions for producing propagating brush discharges (PBDs) above charged polyester and polycarbonate films with grounded metal backing. Having found the breakdown voltage of the film, the latter was corona-charged to a known potential. A spherical electrode was then used to initiate a discharge. It was found that film breakdown voltage increases steeply with thickness as expected, while fabrics and woven materials break down more easily owing to porosity. A second finding was that the critical surface charge density for PBDs was dependent on thickness (increasing rapidly at smaller thicknesses) and the data were material dependent. It was determined that the minimum charge transferred in a PBD is about 10^{-5} C, and that the appropriate test criterion is the breakdown voltage. Figure G.3 shows the region above which it was invariably possible to produce PBDs. The minimum breakdown voltage is about 4 kV, hence to avoid the phenomenon plastic surfaces at risk should be designed to have a breakdown voltage less than this value.

PBDs are not produced by materials containing pores such as layers of dust or from thin layers of lacquer or enamel [74]. Also, to obtain the requisite high charge densities, large quantities of product must be involved such as in pneumatic powder transfer, charged non-conductive liquid transfer in plastic pipe, or rapid emptying of powders from bulk plastic bags (flexible intermediate bulk containers, FIBCs). The latter does not necessarily produce PBDs, and depends on the type of bag and product. For example, flow properties determine the charging on FIBC outlet spouts and many fine powders "rathole" out of the spout with little surface contact or net charge transfer. The PBD phenomenon does not occur during 25 kg sack emptying, although brush discharges might be produced. The latter may ignite flammable vapors but not dusts (excluding extremely sensitive dusts or hybrid mixtures).

Figure G.3 : Limit Curves for Propagating Brushes from Charged Polyester and Polycarbonate Films



APPENDIX H : ELECTROSTATIC MODELS AND APPLICATIONS

The accumulation of charge in vessels and the attendant potentials and fields are discussed. Analytical models are described for simple geometries. Charge accumulation on non-conductive surfaces such as plastics is discussed in terms of image charge effects, charge transfer measurement, charge density measurement fields and potentials. This is extended to the case of plastic layers on metal substrates and other cases where propagating brush discharges may be produced. The capacitance of simple objects is discussed with practical examples.

Charge Accumulation in Tanks

One can consider a tank with any number of inlet and outlet lines. Of the charge flowing through the inlet lines, some will relax in the tank and some will flow out. The change of charge with time can be readily expressed in terms of currents to and from the tank:

$$dQ/dt = \Sigma I_{in} - \Sigma I_{out} - Q/\tau \qquad \text{(H.1a)}$$

The latter term is the rate expression for exponential charge relaxation, which strictly holds only for a full tank.

If there is only one inlet line and no outflowing liquid:

$$dQ/dt = I_S - Q/\tau \qquad \text{(H.1b)}$$

where I_S is a constant streaming current to the tank. Integrating:

$$Q_t = I_S \cdot \tau + (Q_o - I_S \cdot \tau) \cdot \exp(-t/\tau) \qquad \text{(H.1c)}$$

If the tank is initially empty, $Q_o = 0$ and the expression reduces to:

$$Q_t = I_S \cdot \tau \{1 - \exp(-t/\tau)\} \qquad \text{(H.1d)}$$

Hence for liquid flowing into an initially empty, conductive tank the charge "Q_t" and charge density "S_t" remaining at any time is given approximately by the "leaky capacitor" equation:

$$Q_t = I_S \cdot R \cdot C \{1 - \exp.(-t/RC)\} \qquad \text{(H.1e)}$$

since $\tau = R \cdot C = \varepsilon_o \cdot \varepsilon_r / \sigma$ (relaxation time constant)

Now $S = Q/V$ (charge density)

so $S_t = (I_S \cdot \tau / V) \cdot \{1 - \exp(-t/\tau)\}$ (C/m^3) (H.2)

where I_S = streaming current to tank (amperes)
V = volume of tank (m^3)

Complications are that in practice V is not constant as a tank is being filled. However, the approximate relation holds fairly well for partly filled tanks provided the contents are well stirred.

The streaming current to the tank I_S can be expressed in terms of flow rate f (m^3/s) and incoming charge density S_o:

$$S_t = (S_o \cdot f \cdot \tau / V) \{1 - \exp(-t / \tau)\} \quad (H.3)$$

For a typical hydrocarbon with $\varepsilon_r = 2$, substitution can be made for the relaxation time constant $\tau \sim 18 / \sigma$. For a large tank in which the filling time t is much longer than τ, the expression reduces to:

$$S_t = S_o \cdot f \cdot \tau / V \sim 18 \cdot S_o \cdot f / (V \cdot \sigma) \quad (H.4)$$

Fields and Potentials within Vessels

The field (E) and potential (Φ) are found by solution of the Laplace equation in regions without space charge and by solution of the Poisson equation in regions with space charge. Analytical solution is possible only for simple geometries such as spheres and cylinders; even in these cases if the contents are not uniformly charged the solutions take the form of series. For more complex geometries such as tanks containing internals only computer methods can be used.

Laplace's equation: $\nabla^2 \Phi_v = 0 \quad (H.5)$

Poisson's equation: $\nabla^2 \Phi_L = - S/(\varepsilon_o \varepsilon_r) \quad (H.6)$

where $S \equiv$ charge density ($C.m^{-3}$)

$\varepsilon_r \equiv$ dielectric constant

(1) Simple Geometries with Homogeneous Space Charge

Simple geometrical cases are considered in [1]: infinite parallel plates, sphere, infinite cylinder and coaxial infinite cylinders. When the internal space charge is uniform all of these cases reduce to one dimensional variation of potential and field, owing to the symmetry. Series approximations from analytical methods, or numerical computation can be applied to less simple geometries such as cubes and rectangular spaces.

Infinite Parallel Plates

Unlike the case of a parallel plate capacitor, where charge is held on the plates, the boundary condition here is that the plates are at ground potential. For a uniform space charge density "S" the plane of symmetry is midway between the plates and is used as the origin x=0. Hence $\Phi = 0$ at $x = \pm d$, where d is half the plate separation, and $\Phi = \Phi_{max}$ at x=0. From the one dimensional form of Poisson's equation:

$$d^2\Phi/dx^2 = - S/(\varepsilon_o \varepsilon_r) \quad (H.7)$$

hence $$E = - d\Phi/dx = Sx/(e_o e_r) \quad (H.8)$$

The maximum field E_{max} occurs at the boundaries where $x = \pm d$:

$$E_{max} = \pm Sd/(\varepsilon_o\varepsilon_r) \quad (H.9)$$

From H.7: $$\Phi = S\,(d^2 - x^2) / (2\varepsilon_o\varepsilon_r) \quad (H.10)$$

The maximum potential Φ_{max} occurs midway between plates where x = 0:

$$\Phi_{max} = S \cdot d^2 / (2\varepsilon_o\varepsilon_r) \quad (H.11)$$

These equations give a crude approximation of field and potential in containers with a large ratio of width to depth.

Sphere

From Poisson's equation the potential in a grounded metal sphere containing uniform space charge density "S" is:

$$\Phi(r) = S\,(R^2 - r^2) / (6\varepsilon_o\varepsilon_r) \quad (H.12)$$

where R = sphere radius
r = distance from center of sphere

The maximum potential is at the center of the sphere where r = 0:

$$\Phi_{max} = SR^2 / (6\varepsilon_o\varepsilon_r) \quad (H.13)$$

The minimum potential is at the grounded wall where $\Phi = 0$.

By differentiating (H.12) the electric field is:

$$E(r) = S\,r / (3\varepsilon_o\varepsilon_r) \quad (H.14)$$

The maximum field is at the grounded wall where r = R:

$$E_{max} = S\,R / (3\varepsilon_o\varepsilon_r) \quad (H.15)$$

Infinite Cylinder

From Poisson's equation the potential in an infinitely long grounded cylinder containing uniform space charge "S" is:

$$\Phi(r) = SR^2\,(1 - r^2/R^2) / (4\varepsilon_o\varepsilon_r) \quad (H.16)$$

where R = cylinder inside diameter
r = distance from axis

The maximum potential is on the axis where r = 0:

$$\Phi_{max} = SR^2 / (4\varepsilon_o\varepsilon_r) \quad (H.17)$$

By differentiating (H.16) the electric field is:

$$E(r) = Sr / (2\varepsilon_o\varepsilon_r) \quad \text{(H.18)}$$

The maximum field is at the grounded wall where r = R:

$$E_{max} = SR / (2\varepsilon_o\varepsilon_r) \quad \text{(H.19)}$$

Coaxial Infinite Cylinders

As shown in [1] the solution for potential between coaxial cylinders of respective radii R_i (inner) and R_o (outer) containing a uniform space charge density "S" in terms of distance from axis of symmetry "r" is:

$$\Phi = SR^2\{(1 - r^2/R^2) - \{1 - R_i^2/R^2)\,(\ln (r/R)\} / \ln (R_i/R))\} / (4\varepsilon_o\varepsilon_r) \quad \text{(H.20)}$$

The boundary conditions being $\Phi = 0 @ r = R_i$

$\Phi = 0 @ r = R_o$

The field is given by $- d\Phi / dr$:

$$E = SR\,\{2r / R_o + ((1 - (R_i / R_o)^2) / (r / R_o \ln (R_i/R_o))\} / (4\varepsilon_o\varepsilon_r) \quad \text{(H.21)}$$

The maximum potential occurs at:

$$(r/R)_m = - (1 - (R_i / R_o)^2) / (2 \ln (R_i / R_o)$$

$$\Phi_{max} = SR^2[1 + \{(1 - P^2) / (2\ln P)\}\{1 - \ln \{- (1- P^2) / (2\ln P)\}] / (4\varepsilon_o\varepsilon_r) \quad \text{(H.22)}$$

$$P = R_i / R$$

The maximum fields occur at the boundaries:

$$E_i = SR\{2P + (1 - P^2) / (P \ln P)\} / (4\varepsilon_o\varepsilon_r) \quad \text{(H.23)}$$

$$E_o = SR\{2 + ((1 - P^2) / \ln P)\} / (4\varepsilon_o\varepsilon_r) \quad \text{(H.24)}$$

Klinkenberg [1] considered the case where the inner radius R_i is much smaller than the outer radius R_o, for example a wire running along the axis of a cylinder of much larger large diameter such as a pipeline or tank. In this case where P and P^2 are much less than unity, ln P remains significant or greater than unity. With the P and P^2 terms << 1, the boundary fields become:

$$E_i = SR / (4\varepsilon_o\varepsilon_r P \ln P) \quad \text{(H.25)}$$

$$E_o = SR\,\{2 + (1 / \ln P)\} / (4\varepsilon_o\varepsilon_r) \quad \text{(H.26)}$$

As $P \rightarrow 0$ the field E_o goes to $(SR / (2\varepsilon_o\varepsilon_r)$, the same as equation (H.19) for a single cylinder.

As $P \rightarrow 0$ the ratio of these fields:

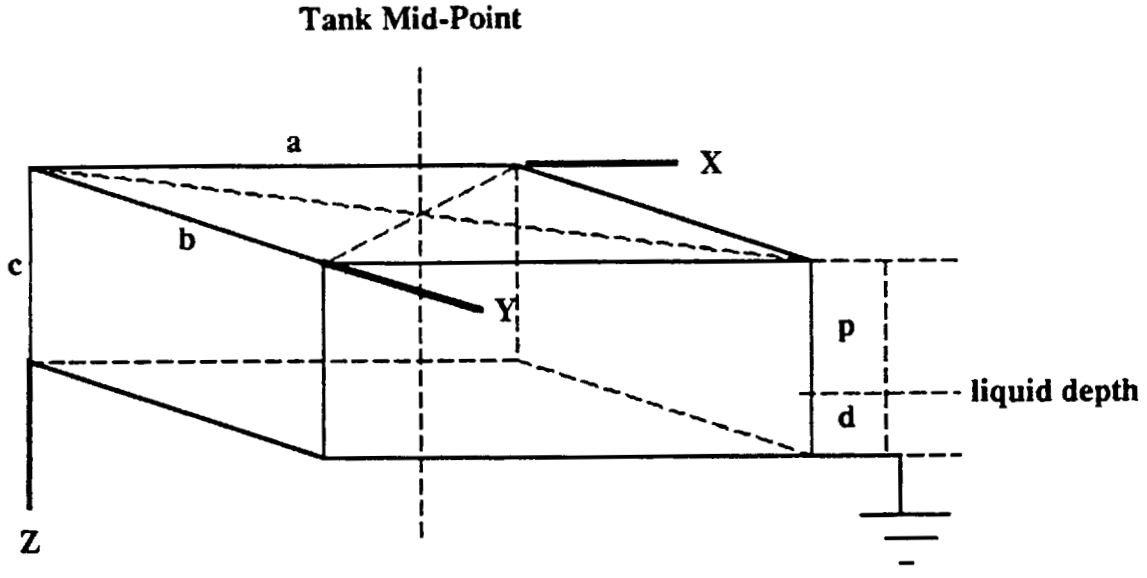
$$E_i / E_o \quad \rightarrow \quad 1 / (2P\ln P) \qquad \text{(H.27)}$$

Thus as discussed in [1] the wire increases the maximum field roughly by the factor (1 / (2PlnP) relative to the cylinder alone. This is significant in the use of such wires as static neutralizers. Klinkenberg gives the example of a 1.5 mm wire on the axis of a 6 inch pipe containing a space charge of 1 $\mu C/m^3$. The maximum potential and field are respectively 52 V and 23 kV/m. With the wire absent they are 79 V and 2.1 kV/m. The inner conductor therefore depresses the space potential to a small degree relative to the very large increase in maximum field.

Rectangular and Cubic Geometries

Using the approach of Carruthers and Wigley [39], who derived approximate expressions for fields and potentials in cubical tanks uniformly filled with charged mist, it is simple to derive the general expressions for rectangular tanks completely filled with uniform charge density. The geometry is given in Figure H.1 where "d" (depth of liquid in tank) is zero:

Figure H.1 : Co-ordinate System for Rectangular Tanks



From Poisson's Equation (H.6) and the boundary condition that the potential $\Phi = 0$ over the tank walls, we try a solution of form:

$$\Phi = \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} B(l,m,n) \sin(\pi lx/a) \cdot \sin(\pi my/b) \cdot \sin(\pi nz/c) \qquad \text{(H.28)}$$

(l,m,n odd)

To find the form of B this is substituted back into Poisson's Equation (H.6) and we find the potential to be of the form:

$$\Phi = - \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{64a^2b^2c^2S}{\varepsilon_o\varepsilon_r\pi^5 lmn\,(b^2c^2l^2 + a^2c^2m^2 + a^2b^2n^2)} \times \sin(\pi lx/a) \cdot \sin(\pi my/b) \cdot \sin(\pi nz/c) \qquad \text{(H.29)}$$

(l,m,n odd)

If for a first approximation only the first term in the series is taken (l=m=n=1):

$$\Phi \approx (\beta / \pi) \cdot \sin(\pi x/a) \cdot \sin(\pi y/b) \cdot \sin(\pi z/c) \qquad \text{(H.30)}$$

where $$\beta = 64a^2b^2c^2S / \{\varepsilon_o\varepsilon_r\pi^4 (b^2c^2 + a^2c^2 + a^2b^2)\} \qquad \text{(H.31)}$$

Maximum Potentials and Fields

From (H.30) and (H.31) the relationship between charge density "S" and the fields and potentials in the tank can be found. For example, the maximum potential is in the center of the tank where x/a = y/b = z/c = 0.5 and the sine terms in (H.30) are unity:

$$\Phi_m \approx \beta / \pi \quad \text{(H.32)}$$

To find the electric fields (H.30) is differentiated with respect to x,y and z in turn and multiplied by minus 1:

$$E_x \approx (\beta / a)\cdot\cos(\pi x/a)\cdot\sin(\pi y/b)\cdot\sin(\pi z/c) \quad \text{(H.32)}$$

$$E_y \approx (\beta / b)\cdot\sin(\pi x/a)\cdot\cos(\pi y/b)\cdot\sin(\pi z/c) \quad \text{(H.33)}$$

$$E_z \approx (\beta / c)\cdot\sin(\pi x/a)\cdot\sin(\pi y/b)\cdot\cos(\pi z/c) \quad \text{(H.34)}$$

The greatest electric fields occur at the center of each face of the enclosure and are of magnitude:

$$E_{x,m} \approx \beta / a \quad \text{(H.35)}$$

$$E_{y,m} \approx \beta / b \quad \text{(H.36)}$$

$$E_{z,m} \approx \beta / c \quad \text{(H.37)}$$

Cube Case

In the case of a cubical enclosure a = b = c and the maximum potential and field, respectively at the center of each face and in the tank center are (from H.32 and H.35):

$$\Phi_m \approx 64a^2S / (3\varepsilon_o\varepsilon_r\pi^5 a) \quad \text{(H.38)}$$

$$E_m \approx 64aS / (3\varepsilon_o\varepsilon_r\pi^4) \quad \text{(H.39)}$$

Cube : Estimate from Computer Modeling

It has been shown [56] using finite element computer modeling that the maximum space potential Φ_m and boundary field (E_m) in a cubical compartment of side "a" containing uniform charge density "S" are:

$$\Phi_m = 0.056\cdot S\cdot a^2 / (\varepsilon_o\varepsilon_r) \quad \text{(H.40)}$$

$$E_m = 0.28\cdot S\cdot a / (\varepsilon_o\varepsilon_r) \quad \text{(H.41)}$$

The field can be compared with the approximate solution derived in (H.39) for a cube:

$$E_m \approx 64\cdot S\cdot a / (3\varepsilon_o\varepsilon_r\pi^4) \approx 0.22\cdot S\cdot a / (\varepsilon_o\varepsilon_r)$$

The error for the approximate solution is (-) 21% taking only the first term of the series solution. This error is small for applications such as tank washing where the charge density will not be known accurately and the dielectric constant will normally be assumed to be unity.

(2) Vertical Cylindrical Geometry : Charged Liquid plus Uncharged Vapor Space

The model [7,44] is for a grounded conducting cylindrical container being filled with a charged liquid of low conductivity. An analytical solution to the electrostatic potential inside the vapor region is presented in the form of a convergent series of Bessel functions and hyperbolics. The model assumes that the liquid is uniformly charged, even at the surface, with a constant incoming charged density that relaxes in a manner described by equation A.6. An approximate form will be derived for the maximum potential given the cylinder dimensions, the liquid depth, conductivity and dielectric constant, and the incoming charge density. A similar forms are given for the electric field strength.

Potential

Derivation of the electrostatic potential is carried out by solving the Laplace equation for the vapor region, where there is assumed to be no net charge, and the Poisson equation for the liquid region which contains a net charge determined by the charge density. The boundary conditions are such that the potential goes to zero at the grounded conducting walls and that the potential and its normal displacements are continuous at the vapor-liquid interface. The time dependence of the charge density is assumed to be completely separable and is treated separately.

Consider a cylindrical container with a radius **b** and and height **c** filled with a liquid to a depth **d**, giving a vapor depth of **p** = **c**-**d**, as shown in Figure H.2.

Figure H.2. Cylindrical Container of Height c and Radius b filled to Depth d.

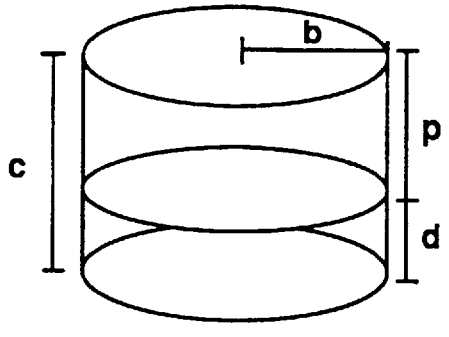
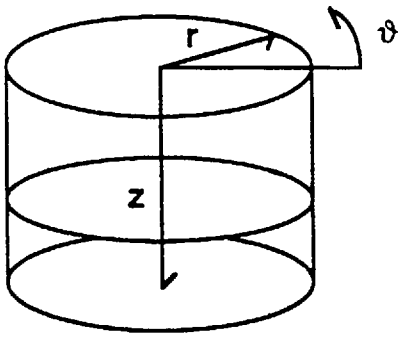


Figure H.3. Cylindrical Coordinate System.



Using the terminology in [7], general solution of Laplace's equation in the vapor region gives:

$$\Phi_V = \sum_{m=1}^{\infty} \alpha_m J_0(\lambda_{0m} r) \sinh(\lambda_{0m} z) \qquad \text{(H.42)}$$

where $\lambda_{0m} = \rho_{0m} / b$ and $J_0(\rho_{0m}) = 0$

The α terms will be found by matching boundary conditions at the vapor-liquid interface. General solution of Poisson's equation in the liquid region gives:

$$\Phi_L = \{S(b^2 - r^2) / (4 \varepsilon_o \varepsilon_L)\} - (S/\varepsilon_o\varepsilon_L) \sum_{m=1}^{\infty} J_2(\lambda_{0m} b) J_0(\lambda_{0m} r) / \lambda^2_{om}$$

$$[\cosh(\lambda_{0m} z) - \gamma_m \sinh(\lambda_{0m} z)] / [\cosh(\lambda_{0m} c) - \gamma_m \sinh(\lambda_{0m} c)] \qquad \text{(H.43)}$$

At the liquid surface the boundary conditions for the vapor and liquid regions should match. That is, the potential and normal displacements should be continuous. Following substitution for the γ terms, found from the normal displacement boundary condition, these considerations [7] allow the α terms to be expressed as:

$$\alpha_m = (S/\varepsilon_o)[J_2(\lambda_{0m} b)/ \lambda^2_{0m} J_1^2(\lambda_{0m} b)] [\cosh(\lambda_{0m} d) - 1] /$$

$$[\varepsilon_L \cosh(\lambda_{0m} d)\sinh(\lambda_{0m} p) + \varepsilon_V \sinh(\lambda_{0m} d)\cosh(\lambda_{0m} p)] \qquad \text{(H.44)}$$

Approximations

The potential at any given point (r,z,ϑ) can be determined for a given radius (**b**), height (**c**), depth (**d**), charge density (**S**), and dielectric constants (ε_r, ε_V). However, the general vapor region solution is in principle infinite and the α coefficients are nontrivial for a hand calculation. In order for the analytical solution to be of very much use, the series must converge reasonably quickly. It would also be useful to simplify the coefficients further.

The vapor region series solution is fairly well behaved, with the first term being the dominant one and an upper limit to the sum. At the point of maximum potential, which is at the center of the liquid surface, the first term is almost uniformly 10% higher than the actual sum. Likewise, for the field strength, which is addressed later, the first term is almost uniformly 20% higher that its sum. A study of the first 20 terms for the vapor region demonstrated [7] a fairly quickly converging alternating series, with more terms needed at the liquid surface than above it. A reasonable approximation therefore is representation by the first term times a uniform weight factor, κ ($\cong 0.9$), that is:

$$\Phi_V \cong \kappa\,(S/\varepsilon_0)[J_2(\lambda_{01}\mathbf{b})/\lambda^2_{01}\,J_1^2(\lambda_{01}\mathbf{b})]\,J_0(\lambda_{01}\mathbf{r})\,\sinh(\lambda_{01}\mathbf{z})\,[\cosh(\lambda_{01}\mathbf{d}) - 1]\,/$$

$$[\varepsilon_L\cosh(\lambda_{01}\mathbf{d})\sinh(\lambda_{01}\mathbf{p}) + \varepsilon_V\sinh(\lambda_{01}\mathbf{d})\cosh(\lambda_{01}\mathbf{p})] \qquad \text{(H.45)}$$

Maximum Potential at Liquid Surface (Φ_m)

The Mean Value Theorem, the boundary conditions, and the symmetry alone indicate that the maximum potential occurs at the center of the liquid surface. The above approximation at this point (**r**=0, **z**=**p**) is given by:

$$\Phi_m \cong \kappa\,(S/\varepsilon_0)[J_2(\lambda_{01}\mathbf{b})/\lambda^2_{01}\,J_1^2(\lambda_{01}\mathbf{b})]\,\sinh(\lambda_{01}\mathbf{p})\,[\cosh(\lambda_{01}\mathbf{d}) - 1]\,/$$

$$[\varepsilon_L\cosh(\lambda_{01}\mathbf{d})\sinh(\lambda_{01}\mathbf{p}) + \varepsilon_V\sinh(\lambda_{01}\mathbf{d})\cosh(\lambda_{01}\mathbf{p})] \qquad \text{(H.46)}$$

Realizing that $\lambda_{01} \cong \rho_{01}/\mathbf{b}$, and that [45]:

ρ_{01}	=	2.4
$J_1(\rho_{01})$	=	0.52
$J_2(\rho_{01})$	=	0.43

we have:

$$\Phi_m \cong \kappa\,(S/\varepsilon_0)(0.31)\mathbf{b}^2\,\Gamma(\mathbf{d}) \qquad \text{(H.47)}$$

$$\Gamma(\mathbf{d}) \cong [\cosh(2.4\ \mathbf{d}/\mathbf{b}) - 1]\sinh(2.4\mathbf{p}/\mathbf{b})/$$

$$[\varepsilon_L\cosh(2.4\ \mathbf{d}/\mathbf{b})\sinh(2.4\ \mathbf{p}/\mathbf{b}) + \varepsilon_V\sinh(2.4\ \mathbf{d}/\mathbf{b})\cosh(2.4\ \mathbf{p}/\mathbf{b})] \qquad \text{(H.48)}$$

$\Gamma(\mathbf{d})$ is a "form factor", or filling profile for a particular container geometry (and liquid dielectric constant), which goes to zero at the beginning and end of filling. S is the uniform charge density of the liquid. For a charged liquid obeying an exponential law of charge relaxation, as given by equation H.3:

$$\mathbf{S} \equiv (\mathbf{I_S}\tau/\mathbf{V})(1 - e^{-\mathbf{t}/t})$$

and

$$\mathbf{I_S} = \mathbf{S_o}\,\mathbf{f} \quad \text{(Charging current)}$$

$$t = \varepsilon_o\varepsilon_r/\sigma \quad \text{(Relaxation time)}$$

$$\mathbf{V} = \mathbf{d}\mathbf{b}^2\pi \quad \text{(Volume of liquid)}$$

$$\mathbf{t} = \mathbf{V}/\mathbf{f} \quad \text{(Time)}$$

The approximations are most valid at times significantly greater than the relaxation time (τ) and at volumes less than about 90% full. The charge relaxation equation is most valid for liquid conductivities above 2 pS/m. At lower conductivities, charge relaxation is better described by equation A.10. However, the relaxation behavior given by equation A.10 can satisfactorily be simulated by assuming exponential relaxation governed by an effective conductivity of 0.5 pS/m (see figure A.1). For a steady-state charge density model, S would be a constant throughout the filling time.

Approximate Vapor Space Potentials in Terms of Φ_m

If the potential is known at the maximum point, then a single-term expansion allows the potential at any other point to be approximated by

$$\Phi_v(\mathbf{r},\mathbf{z}) \equiv \Phi_m J_0(2.4\mathbf{r}/\mathbf{b}) \sinh(2.4\mathbf{z}/\mathbf{b})/\sinh(2.4\mathbf{p}/\mathbf{b}) \qquad \text{(H.49)}$$

This equation can be used for estimating the off-axis potential. For example, at the dip pipe location in a typical 55 gallon drum configuration, the surface potential is about half the axial value.

Electric Field

The electric field components are derived from the general solution for vapor region potential:

$$E_z = -\sum_{m=1}^{\infty} \alpha_m \lambda_{0m} J_0(\lambda_{0m}r) \cosh(\lambda_{0m}z) \qquad \text{(H.50)}$$

$$E_r = \sum_{m=1}^{\infty} \alpha_m \lambda_{0m} J_1(\lambda_{0m}r) \sinh(\lambda_{0m}z) \qquad \text{(H.51)}$$

Approximations

With arguments similar to those used above, these equations can reasonably well be approximated by:

$$E_z \equiv -\kappa'(S/\varepsilon_0)[J_2(\lambda_{01}b)/\lambda_{01} J_1^2(\lambda_{01}b)] J_0(\lambda_{01}r) \cosh(\lambda_{01}z)$$
$$[\cosh(\lambda_{01}d) - 1]/$$
$$[\varepsilon_L \cosh(\lambda_{01}d)\sinh(\lambda_{01}p) + \varepsilon_V \sinh(\lambda_{01}d)\cosh(\lambda_{01}p)] \quad (H.52)$$

$$E_r \equiv \kappa'(S/\varepsilon_0)[J_2(\lambda_{01}b)/\lambda_{01} J_1^2(\lambda_{01}b)] J_1(\lambda_{01}r) \sinh(\lambda_{01}z)$$
$$[\cosh(\lambda_{01}d) - 1]/$$
$$[\varepsilon_L \cosh(\lambda_{01}d)\sinh(\lambda_{01}p) + \varepsilon_V \sinh(\lambda_{01}d)\cosh(\lambda_{01}p)] \quad (H.53)$$

where κ' is weight factor of about 0.8. Similarly one can show that the maximum field strength is given by:

$$E_{max} = |E_z| \quad \text{at} \quad (r=0, z=p)$$

which becomes

$$E_{max} \equiv \kappa'(S/\varepsilon_0)[J_2(\lambda_{01}b)/\lambda_{01} J_1^2(\lambda_{01}b)] \cosh(\lambda_{01}p)$$
$$[\cosh(\lambda_{01}d) - 1]/$$
$$[\varepsilon_L \cosh(\lambda_{01}d)\sinh(\lambda_{01}p) + \varepsilon_V \sinh(\lambda_{01}d)\cosh(\lambda_{01}p)] \quad (H.54)$$

or in terms of $\Gamma(d)$ defined above:

$$E_{max} \equiv \kappa'(S/\varepsilon_o)(0.75)b\, \Gamma(d)/\tanh(2.4p/b) \quad (H.55)$$

Likewise, the field strength at the top of the container is given by:

$$E_o \equiv \kappa'(S/\varepsilon_o)(0.75)b\, \Gamma(d)/\sinh(2.4p/b) \quad (H.56)$$

If the maximum potential is known, then:

$$E_{max} \equiv (\kappa'/\kappa)(2.4/b)\, \Phi_m/\tanh(2.4p/b) \quad (H.57)$$
$$E_o \equiv (\kappa'/\kappa)(2.4/b)\, \Phi_m/\sinh(2.4p/b) \quad (H.58)$$
hence $$E_o \equiv E_{max}/\cosh(2.4p/b) \quad (H.59)$$

and $E_r \cong E_o J_1(2.4r/b) \sinh(2.4z/b)$ (H.60)

$E_z \cong -E_o J_o(2.4r/b) \cosh(2.4z/b)$ (H.61)

Figure H.4 : Theoretical Filling of Unlined Drum : Effect of Conductivity

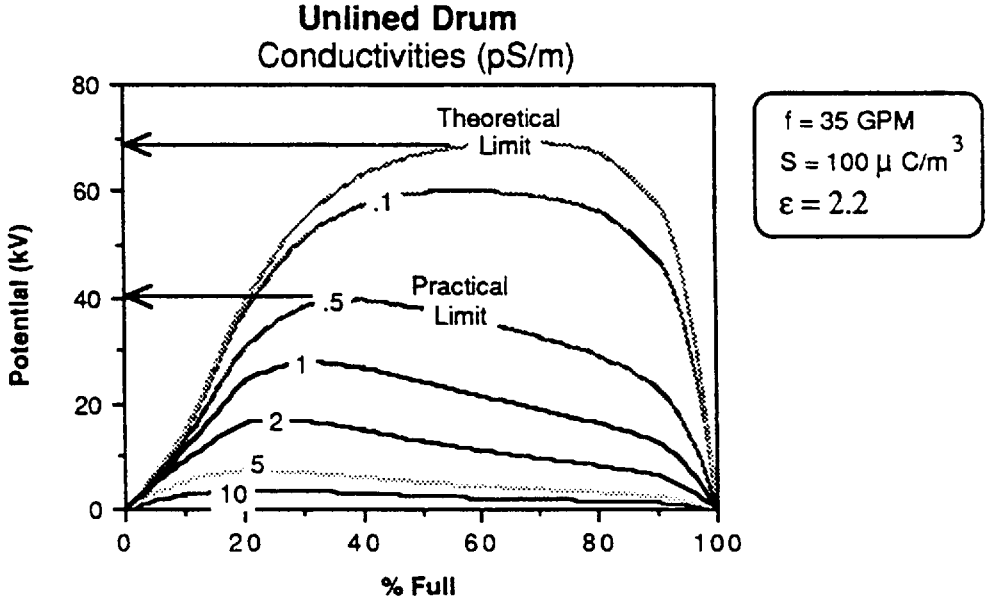


Figure H.5 : Theoretical Filling of Unlined Drum : Effect of Flow Rate

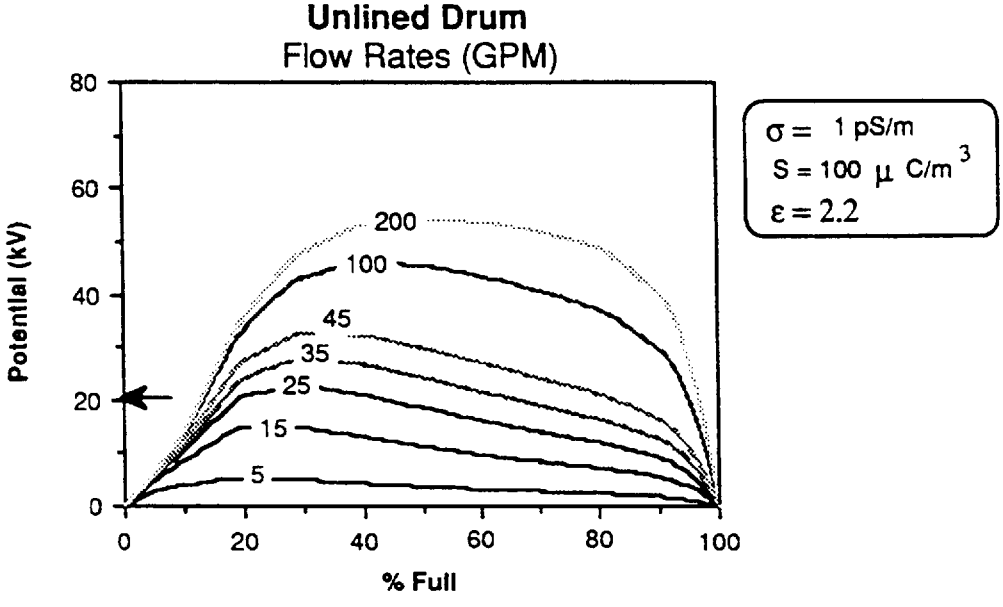
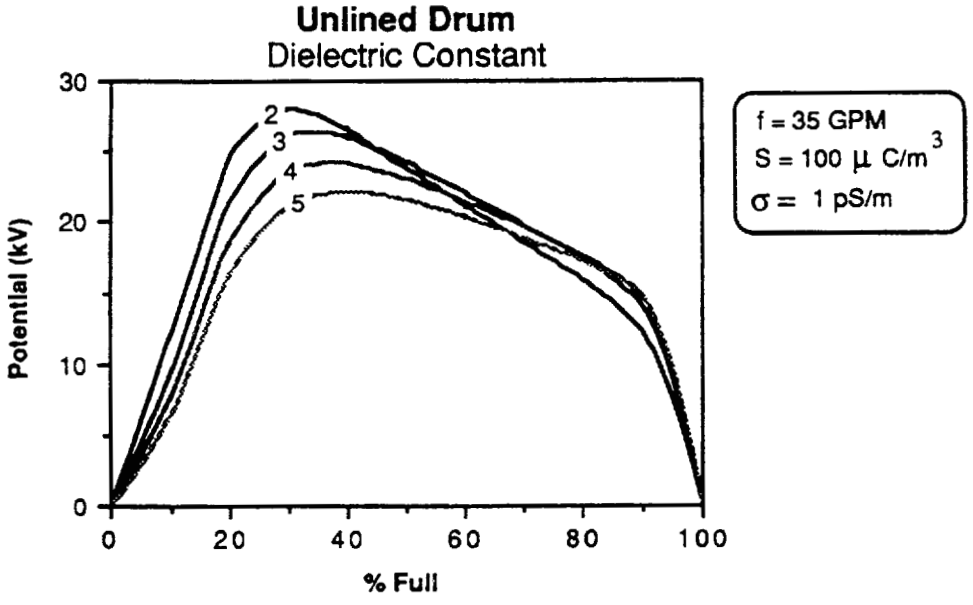


Figure H.6 : Theoretical Filling of Unlined Drum : Effect of Dielectric Constant



(3) Rectangular Geometry with Uncharged Vapor Space

The solution for potential and field in a rectangular tank partially filled with liquid of uniform charge density "S" was derived by Carruthers and Wigley [39]. The system considered (Figure H.1) is a grounded, conductive tank "a" units long, "b" units wide and "c" units in height, filled to depth "d" with non-conductive liquid and leaving an uncharged vapor space to depth (p = c - d). The potential function is derived as a double infinite Fourier series with established convergence. The approach in [39] was to take only the first series term which could lead to position-dependent errors in the calculated field up to a factor of 2.5, although the error is usually smaller and can be readily reduced by summing more series terms.

Subject to the boundary conditions Laplace's equation for the uncharged vapor space and Poisson's equation for the charged liquid-filled space were solved [39] giving the potential solutions for vapor (Φ_v) and liquid (Φ_L):

$$\Phi_v = \sum_{\substack{l=1 \\ (l,m\ \text{odd})}}^{\infty} \sum_{m=1}^{\infty} K \cdot \sin(\pi l x/a) \cdot \sin(\pi m y/b) \cdot \sinh(\beta z) \qquad \text{(H.62)}$$

$$\Phi_L = \sum_{\substack{l=1 \\ (l,m\ \text{odd})}}^{\infty} \sum_{m=1}^{\infty} \{H \cdot \sinh \beta z + F \cdot \cosh \beta z + \alpha/\beta^2\} \cdot \sin(\pi l x/a) \cdot \sin(\pi m y/l) \qquad \text{(H.63)}$$

where:

$$\alpha = 16S / (\varepsilon_0 \varepsilon_L l m \pi^2) \qquad \text{(H.64)}$$

$$\beta = \pi / (l^2/a^2 + m^2/b^2)^{0.5} \quad \text{(H.65)}$$

$$F = K \cdot \sinh \beta p \cdot \cosh \beta p \, (1 - \varepsilon_v/\varepsilon_L) - \alpha \cdot \cosh (\beta p/\beta^2) \quad \text{(H.66)}$$

$$H = (K / \varepsilon_L) \cdot (\varepsilon_o \cdot \cosh^2 \beta p - \varepsilon_L \cdot \sinh^2 \beta p) + \alpha \cdot \sinh (\beta p/\beta^2) \quad \text{(H.67)}$$

$$K = (\varepsilon_L \alpha /\beta^2) \cdot (\cosh \beta d - 1) / \{\varepsilon_o \cdot \cosh \beta p \cdot \sinh \beta d + \varepsilon_L \cdot \sinh \beta p \cdot \cosh \beta d) \quad \text{(H.68)}$$

These solutions were shown [39] to be convergent and to satisfy both the field equations and the boundary conditions, being the only solution by the uniqueness theorem. The field components in the vapor space were found from the negative differentials of potential in the x, y and z directions:

$$E_x = - \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} (K\pi l/a) \cdot (\sinh \beta z \cdot \cos (\pi lx/a) \cdot \sin (\pi my/b) \quad \text{(H.62)}$$
(l,m odd)

$$E_y = - \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} (K\pi m/b) \cdot (\sinh \beta z \cdot \sin (\pi lx/a) \cdot \cos (\pi my/b) \quad \text{(H.62)}$$
(l,m odd)

$$E_z = - \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} K\beta \cdot \cosh \beta z \cdot \sin (\pi lx/a) \cdot \sin (\pi my/b) \quad \text{(H.62)}$$
(l,m odd)

Approximations

By taking only the first terms of the Fourier expansions (-1=l=m) approximate expressions for potential and z-component field in the vapor space are:

$$\Phi_v = \frac{16S \cdot (\cosh \beta d - 1) \cdot \sinh \beta z \cdot \sin (\pi x/a) \cdot \sin (\pi y/b)}{(\varepsilon_o \pi^2 \beta^2) \cdot \{\varepsilon_o \cdot \cosh \beta p \cdot \sinh \beta d + \varepsilon_L \cdot \sinh \beta p \cdot \cosh \beta d\}} \quad \text{(H.63)}$$

$$E_z = - \frac{16S \cdot \{(\cosh \beta d - 1) \cdot \cosh \beta z \cdot \sin (\pi x/a) \cdot \sin (\pi y/b)\}}{\varepsilon_o \pi^2 \beta \cdot \{\varepsilon_o \cdot \cosh \beta p \cdot \sinh \beta d + \varepsilon_L \cdot \sinh \beta p \cdot \cosh \beta d\}} \quad \text{(H.64)}$$

$$\beta = \pi \cdot (1/a^2 + 1/b^2)^{0.5} \quad \text{(H.65)}$$

Maximum and Observed Electric Fields

The maximum electric field $E_{z,m}$ is at the center of the liquid surface (x=a /2, y=b /2, z=p) where the x and y components of field are zero:

$$E_{z,m} = - \frac{16S \cdot \{(\cosh \beta d - 1) \cdot \cosh \beta p\}}{\varepsilon_o \pi^2 \beta \cdot \{\varepsilon_o \cdot \cosh \beta p \cdot \sinh \beta d + \varepsilon_L \cdot \sinh \beta p \cdot \cosh \beta d\}} \quad \text{(H.66)}$$

If the electric field is measured flush with the center of the tank roof ($x = a/2$, $y = b/2$, $z = 0$), as might be done experimentally, the observed field $E_{z,o}$:

$$E_{z,o} = - \frac{16S \cdot \{(\cosh \beta d - 1)}{\varepsilon_o \pi^2 \beta \cdot \{\varepsilon_o \cdot \cosh \beta p \cdot \sinh \beta d + \varepsilon_L \cdot \sinh \beta p \cdot \cosh \beta d\}} \quad \text{(H.67)}$$

Hence in order to approximately relate the observed field to the maximum field in the tank, one simply multiplies the observed field by the factor (cosh βp).

Maximum Liquid Surface Potential

The minimum charge density to produce brush discharges in such a tank might be estimated knowing the minimum surface potential at which discharges have been demonstrated to occur given the introduction of a grounded probe near to the surfaces of charged test liquids. This is variously reported to be somewhere above 20 kV depending on the test method, as discussed in Appendix I. The maximum surface potential Φ_m is in the center of the liquid surface ($x = a/2$, $y = b/2$, $z = p$) and is given by:

$$\Phi_m = \frac{16S \cdot (\cosh \beta d - 1) \cdot \sinh \beta p}{(\varepsilon_o \pi^2 \beta^2) \cdot \{\varepsilon_o \cdot \cosh \beta p \cdot \sinh \beta d + \varepsilon_L \cdot \sinh \beta p \cdot \cosh \beta d\}} \quad \text{(H.68)}$$

Time Dependent Solutions

As developed for the case of the vertical cylindrical container, time-dependent solutions may be found using the given expressions for charge relaxation and filling rate. Using computer methods a number of series terms may be summed.

Effect of Tank Liners

Wall Capacitance Model

In [7] a simple analysis was made for surface potential in a container with a completely insulating liner. The principal assumption was that filling time is long compared to the effective relaxation time of the liquid, so that at all times the potential is everywhere equal. If the charge is assumed to migrate rapidly to the boundaries and form an equipotential surface, the potential will be determined by the capacitance of the surface layer and the total charge. The capacitance of the total surface will be dominated by that across the liner to the metal walls, and the capacitance of the free surface can be neglected. The model assumes that the container is splash filled, so that charge dissipation and other effects of a filling pipe can be neglected. If the capacitance of the wall layer is assumed due to a very thin layer of charged liquid, the geometry can be neglected and the capacitor modeled as a parallel plate capacitor:

$$C = \varepsilon_o \cdot \varepsilon_r \cdot A / a$$

where	A	=	area of liquid in contact with wall	(m^2)
	a	=	thickness of insulating liner	(m)

In [7] the filling of a polyethylene-lined steel drum was modeled. It was assumed that the drum was splash filled at a constant flow rate and charge density, giving a constant streaming current to the drum. For a drum of radius "b" and liquid depth "d", the area in contact with the liquid is that of the base plus the wetted cylindrical area:

$$A = \pi \cdot b^2 + 2 \cdot \pi \cdot b \cdot d$$

where b = drum radius (m)
d = depth of liquid (m)

For a given elapsed filling time "t" and filling rate "f", the depth of liquid "d" is given by:

$$d = f \cdot t / (\pi \cdot b^2)$$

where f = filling rate (m^3/s)
t = time elapsed during filling (s)

Hence $$C = (\varepsilon_o \cdot \varepsilon_r / a) \cdot (\pi b^2 + 2 \cdot f \cdot t / b)$$

The potential $$\phi = Q / C \quad (V)$$

where Q = total charge loaded (C)
C = total wall capacitance (F)

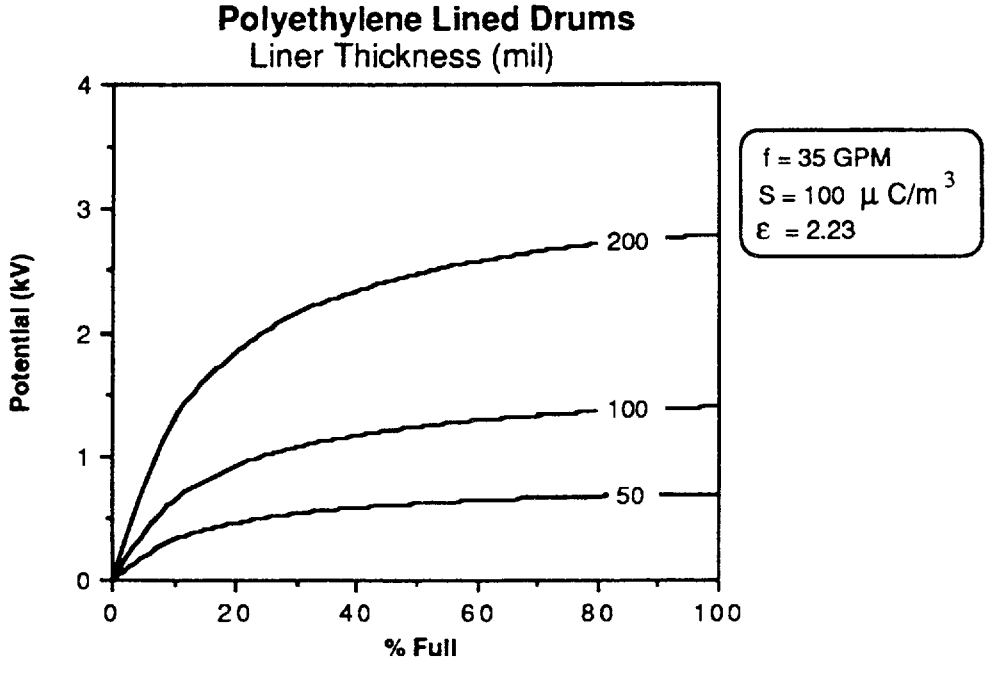
The total charge $$Q = S \cdot f \cdot t \quad (C)$$

where S = charge density (C/m^3)

Hence $$\phi = S \cdot f \cdot t \cdot a \cdot b / \{\varepsilon_o \cdot \varepsilon_r \cdot (\pi b^3 + 2 \cdot f \cdot t)\} \quad (V)$$

The model is shown in Figure H.7 for a typical steel drum being loaded at 35 gpm with liquid having charge density of 100 $\mu C/m^3$ and a dielectric constant of 2.3. Liner thicknesses of 50, 100, and 200 mil are considered (1 mil = 0.001 inch = 25.4 micron).

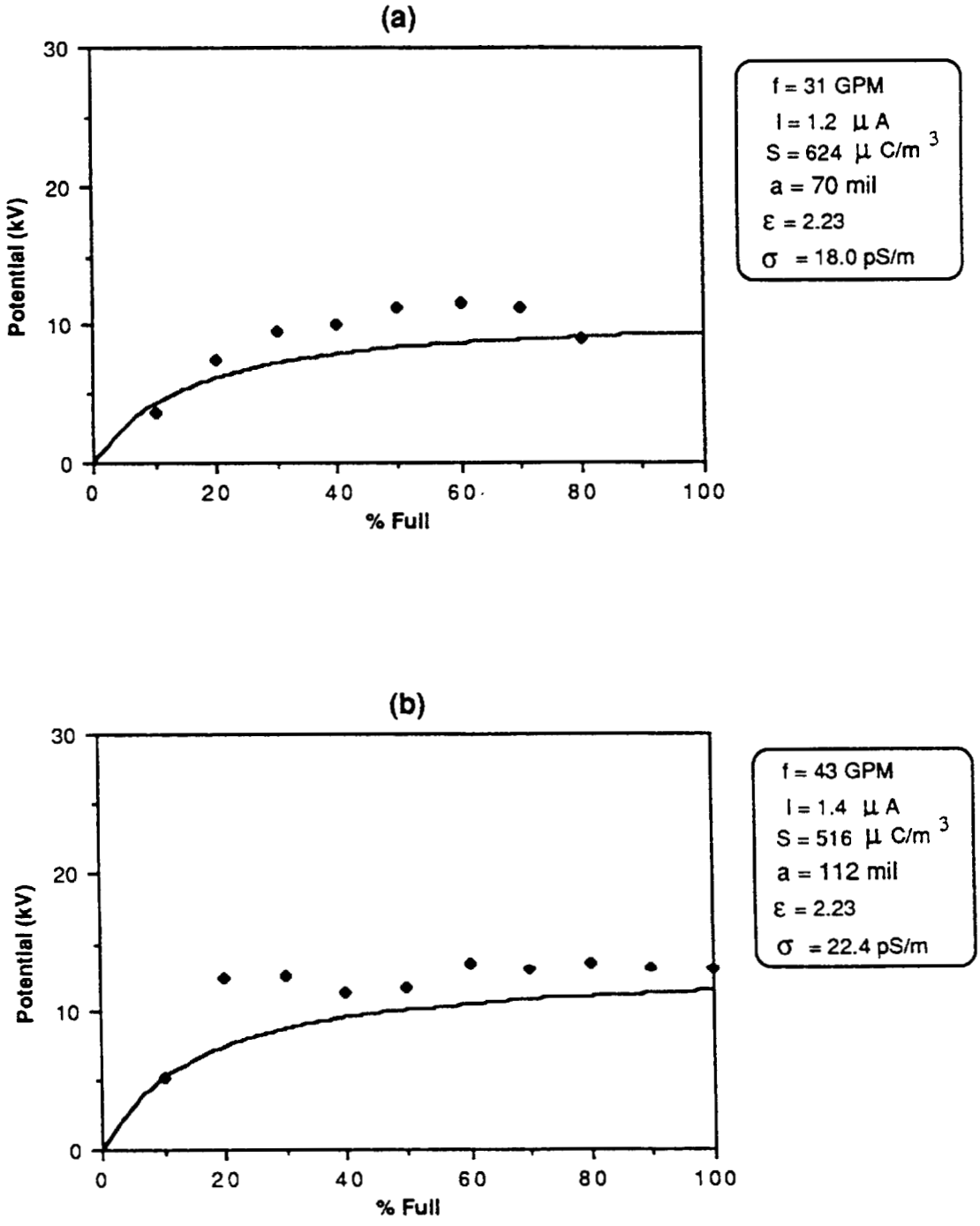
Figure H.7 : Theoretical Filling of Lined Drum : Effect of Liner Thickness



This analysis shows that unless very high charge densities and liner thicknesses are involved, non-conductive liquids whose charge rapidly relaxes to the walls will not give hazardous surface potentials, since incendive brush discharges require at least 25 kV. Conductive liquids can give incendive spark discharges at a few kV and better fit the model assumptions of rapid formation of an equipotential surface. However, such liquids are unlikely to generate the requisite charge densities.

To evaluate the model, experiments were carried out [7] with kerosene having a moderate conductivity of about 20 pS/m, whose relaxation time of about 1 second approximated the assumptions of the model. A close-coupled filter was used to generate high charge densities. Figures H.8 (a) and (b) show typical results compared with the model predictions.

Figure H.8 : Theoretical vs Experimental Potential Profiles for Lined Drum Filling



The agreement was reasonable considering the model neglected the effects of bulk charge plus charge at the free surface.

Application to Lined Road and Rail Tankers

The surface potential approximation should be most accurate for conductive liquids being loaded into a container with a thin, perfectly insulating liner. In this case the accumulation of free surface charge is minimal and the potential should be determined by the capacitance of the wall, since equipotential conditions should be attained very rapidly. A case to consider is the splash-filling of a long, horizontal, lined tank. In the case of a conductive liquid, the maximum safe surface potential will be only a few kV since sparks rather than brush discharges will be produced. This is discussed in the text.

More sophisticated methods including numerical analysis are required for all cases where the rapid formation of an equipotential in the tank cannot be assumed, such as is the case for non-conductive liquids. In this case the principal cause of difficulty is non-uniform charge distribution in the tank. This is a general problem with non-conductive liquids. Charge at the free surface of the liquid has a variable capacitance due to its image charge on the tank walls and roof, which changes during filling. The effect of the liner is far from certain since the charge relaxed to the liner may not be fixed but may be convected away by turbulent eddies. Hence it is uncertain how much charge is in the bulk of the liquid, the wall boundaries and the free surface. Additional problems include hydrodynamic flow uncertainties, including jet and eddy effect that direct highly charged liquid to the free surface, and the effects of froth production during splash filling. The problem of unlined road and rail tankers has been tackled by semi-empirical methods with an emphasis on observation of static discharge thresholds, as discussed in the text. There has been no comparable study of lined tanks.

Computer Modeling

Proprietary and commercially available software has been developed and used to model electrostatic potentials and fields under a variety of situations. One, two and three dimensional methods have been used. The problem with such approaches when applied to dynamic systems such as tank filling is that their accuracy is limited by the need to exactly define the location of charges in the system. Permittivities and complex geometries are a small problem since the former have a small effect (or can be estimated well) and the latter can be modeled using finite element methods, the only limitation being increased computation time as the grid size is decreased.

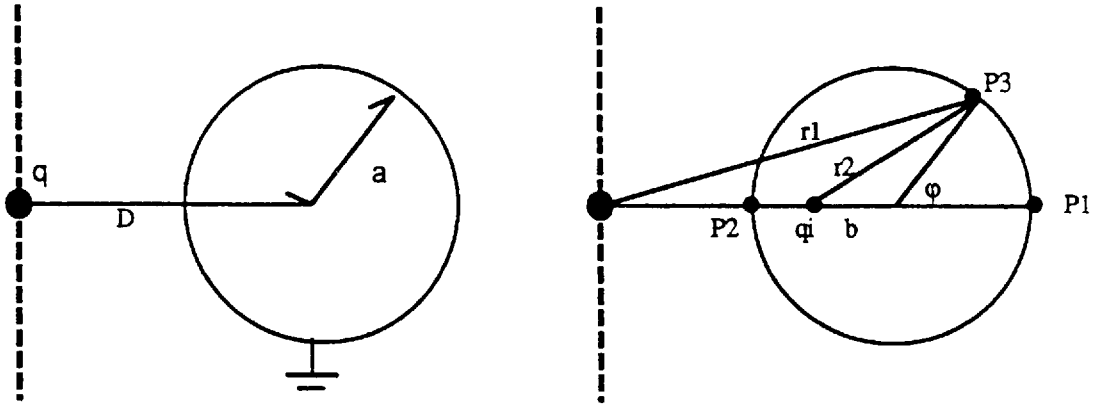
Definition of charge location is especially difficult for powder transfer modeling (for example, silo filling) since there is usually a bimodal charging process leading to changes in polarity in the space charge, both in the compacted bed and in the free space containing falling powder. The problem is simpler for liquids owing to there being only one net sign of charge in the liquid phase and a relatively small space charge in the free space. Polarity changes can be due to froth or mist production. For liquids the main problem as discussed above is the non-uniformity of charge distribution in the liquid and an excess charge at the free surface.

Grounded Spheres Above Charged Plane Insulators

Use of Method of Images to Find Induced Charge on Grounded Sphere

Simplification of the problem is achieved by the method of images. Consider the point charge "q" on the uniformly charged non-conductive surface in Figure H.9. This charge must induce an opposite charge on the surface of the grounded sphere so as to maintain the sphere at ground potential. Using the method of images the real surface charge induced can be simulated by a single imaginary point charge "q_i" inside the sphere that has the same effect; namely, to maintain a zero equipotential surface on the outside of the sphere.

Figure H.9 : Method of Images



If such a charge exists then by symmetry it must lie on the line connecting "q" with the center of the sphere. First, suppose that the charge "q" and image charge "q_i" give zero potential at the points P_1 and P_2. It follows from the definition of potential that:

$$4 \cdot \pi \cdot \varepsilon_0 \Phi(P_1) = q / (D + a) + q_i / (a + b) = 0$$

and $$4 \cdot \pi \cdot \varepsilon_0 \Phi(P_2) = q / (D - a) + q_i / (a - b) = 0$$

hence $$q_i = - a \cdot q / D$$

and $$b = a^2 / D$$

To show that this image charge positioned at "b" gives zero potential at a general point "P_3" :

$$\Phi(P_3) = q / (4 \cdot \pi \cdot \varepsilon_0 \cdot r_1) + q_i / (4 \cdot \pi \cdot \varepsilon_0 \cdot r_2)$$

now $$r_1 = (D^2 + a^2 + 2 \cdot D \cdot a \cdot \cos\varphi)^{0.5}$$

and $$r_2 = (b^2 + a^2 + 2 \cdot b \cdot a \cdot \cos\varphi)^{0.5}$$

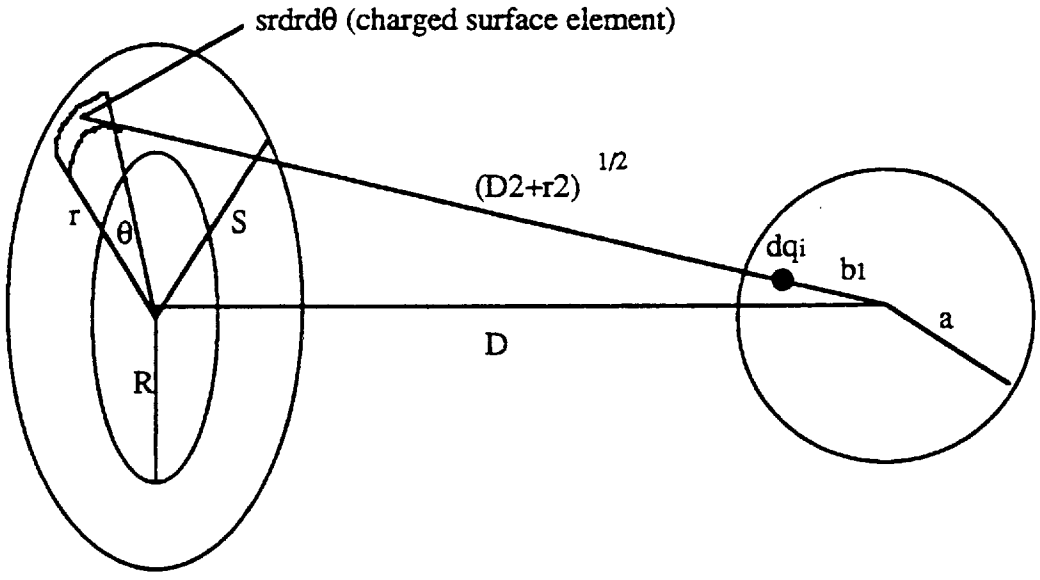
so $$4 \cdot \pi \cdot \varepsilon_0 \cdot \Phi(P_3) = q(D^2 + a^2 + 2Da\cos\varphi)^{-0.5} - (aq/D)(a^4/D^2 + a^2 + 2a^3\cos\varphi/D)^{-0.5}$$

Inspection of the second term on the right hand side shows that it is equal to the first term, and the right hand side is zero, hence $\Phi(P_3) = 0$.

Partial Discharge of Non-Conductive Disc to Grounded Sphere

The analysis can readily be extended to the case of a grounded sphere above the center of a uniformly charged disc which discharges completely up to some arbitrary radius (Figure H.10). Consider first a charged annulus on the disc with surface charge density "s". The disc has radius "S" and the charged region lies between radii R and S. A charged surface element of area r.dr.dθ therefore has a charge s.r.dr.dθ and imposes an image charge dq_i inside the sphere at a distance b_1 from its center, on the line joining the elemental area to the center of the sphere.

Figure H.10 : Grounded Sphere above Charged Non-Conductive Disc



From the relationships established previously for magnitude and location of the image charge:

$$b_1 = a^2 (D^2 + r^2)^{-0.5}$$

$$dq_i = - as (D^2 + r^2)^{-0.5} . r.dr.d\theta$$

The total induced charge on the sphere due to all elements of the annulus can be found by integration:

$$q_i = \int_0^{2\pi} \int_R^S - as (D^2 + r^2) . r.dr.d\theta$$

$$q_i = -2\pi sa \int_R^S r(D^2 + r^2)^{-0.5} dr$$

$$q_i = -2\pi sa \{(D^2 + S^2)^{0.5} - (D^2 + R^2)^{0.5}\}$$

If the disc is uniformly charged all over, not just the annulus between $R < r < S$, then the image charge is found for $R=0$.

The image charge is not located at one point but is distributed over a continuous closed surface inside the sphere. In reality the induced charge will be distributed on the surface of the sphere, but its magnitude will be identical to that of the image charge. This can be seen by considering a Gaussian surface located just outside the sphere. The total flux through this surface must be the same whether the sphere with an induced charge on it is present, or whether this system is replaced by the image charge.

Effect of Image Charge on Detectable Charge Transfer from Disc to Sphere

Suppose one wished to measure the magnitude of a discharge between the charged surface and the sphere by measuring the flow of charge from the sphere to ground (ie, current). In principle this measurement will give the shape of the pulse and, by integration, the charge transferred in the pulse. In practice the measured charge is reduced by the presence of the induced (image) charge, as discussed by Britton and Williams [38]:

Before the discharge the entire surface is uniformly charged. Thus the initial image charge q_{io} can be found as above using R=0:

$$q_{io} = -2\pi sa\{(D^2 + S^2)^{0.5} - D\}$$

This is the total image charge due to a uniformly charged disc and equals the induced charge on the spherical electrode. To get an idea of the magnitude of this induced charge, one can compare it with the total initial charge on the disc ($q_o = s\pi S^2$) and substitute typical values for geometry. Let an electrode of radius a = 1 cm be positioned with its center 10 cm above a charged disc of radius S = 20 cm. In this case D = 10 cm and from:

$$|q_{io}/q_o| = 2a\{(D^2 + S^2)^{0.5} - D\} / S^2$$

It follows $|q_{io}/q_o| = 6.2\%$

The induced charge varies with geometry but is typically of the order 10% or less of the total charge.

Suppose all the charge on the disc contained up to inner radius "R" is discharged. Then, the final image charge q_{if} can be found as above by setting R=R:

$$q_{if} = -2\pi sa\{(D^2 + S^2)^{0.5} - (D^2 + R^2)^{0.5}\}$$

The charge that has been transferred to the sphere "q_t" is:

$$q_t = \pi R^2 s$$

When the discharge occurs, suppose a quantity of charge δ flows to ground through the measuring device. We can now balance the charges on the sphere:

$$q_{if} = q_{io} + \pi R^2 s - \delta$$

Hence $$\delta = 2\pi sa\{D - (D^2 + R^2)^{0.5}\} + \pi R^2 s$$

This equation shows that the measured charge transfer δ is independent of the radius "S" of the charged disc. The ratio of measured charge transfer to the true charge transfer is given by:

$$\delta / q_t = \{R^2 - 2a\{(D^2 + R^2)^{0.5} - D\}\} / R^2$$

This analysis shows that the measured charge transfer can never be equal to the actual charge transfer except where $q_{if} = q_{io}$, that is, either there is no change in image charge during

discharge or the image charge is so small that any change is less than the sensitivity of the measuring device. This can be an important effect for accurate measurement where the geometry makes the image charge a large fraction of the charge transferred and must be considered when measuring charge transfer. In practice, the image charge can be made very small compared with "q_t" by using a special probe. For example, a spherical electrode can contain an isolated detection element which receives the total charge transfer from the discharge. The image charge on this element is a small fraction of the total image charge on the probe.

Limit Cases : Discharge from Disc to Grounded Plate or Pointed Electrode

As the radius of the grounded sphere becomes larger the magnitude of the image charge becomes greater and the fraction of measurable charge flowing to ground becomes smaller. In the limiting case we can consider a grounded circular plate above the charged disc.

The distance between the charged disc and grounded plate d = (D - a). We wish to examine the limit of (δ / q_t) as the sphere diameter becomes infinite.

Now $\delta / q_t = \{R^2 - 2a\{(D^2 + R^2)^{0.5} - D\}\} / R^2$

Substituting $D = d + a$

As $a \rightarrow \infty$ $\delta / q_t \rightarrow 0$

Alternatively, if the electrode is pointed, $a \rightarrow 0$ and $\delta \rightarrow q_t$.

Field and Potential between Charged Non-Conductive Disc and Grounded Sphere

An extension of the approach given above allows electric fields and potentials to be calculated (Figure H.11). This approach was outlined by Heidelberg [67] but the derivation in this German paper is difficult to follow. On the axis of symmetry, the solutions can be obtained analytically.

As before, the magnitude and position of the image charge dQ' due to the element of surface charge dQ is given by:

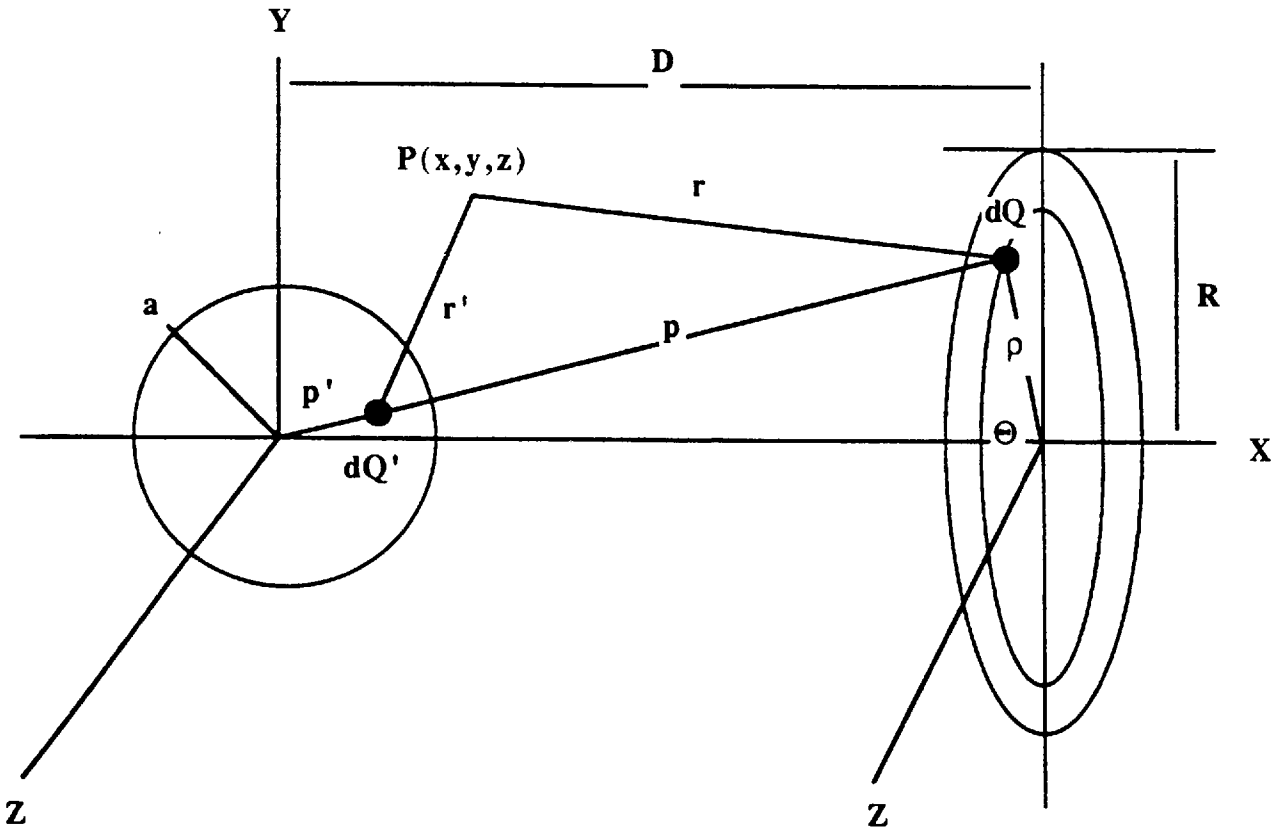
$$dQ' = -(a / p) \cdot dQ$$

and $$p \cdot p' = a^2$$

We can find the equation governing the position of all the image charges dQ'. In the co-ordinate system with center at the mid-point of the sphere the position of any image charge is given by:

$$(p') = x^2 + y^2 + z^2$$

Figure H.11 : Charged Non-Conductive Disc and Grounded Sphere : Geometry for Field and Potential Analysis



For the similar triangles $p' / x = p / D = a^2 / (Dp')$

Hence $(p')^2 = a^2 x / D$

Thus $a^2 x / D = x^2 + y^2 + z^2$

Rearranging and completing the square the location of all image charges dQ' is given by:

$$\{x - a^2 / (2D)\}^2 + y^2 + z^2 = a^4 / (4D^2)$$

Suppose the charge dQ on the disc is due to an element of surface df having charge density "s". The contribution to total potential at some arbitrary point P at distances r and r' respectively due to the charge dQ and its image charge dQ' can be written in terms of df:

$$d\Phi = \{s \cdot df / (4\pi\varepsilon_o)\} \{(1 / r) + (a / pr')\}$$

In order to find the potential at P due to all the charges dQ and image charges dQ' we need to find the quantities r and r' in terms of the geometrical parameters a, R, and D. Summation is done by integrating over the surface from $\rho = 0$ to R and from $\theta = 0$ to 2π.

From the simple geometry it follows that:

$$r = \{(D - x)^2 + (\rho \cdot \sin.\theta - y)^2 + (\rho \cdot \cos.\theta - z)^2\}^{0.5}$$

If we let the co-ordinates of the image charge dQ' be given by x', y', and z', it follows:

$$r' = \{(x - x')^2 + (y - y')^2 + (z - z')^2\}^{0.5}$$

By consideration of the congruent triangles defined by D and p in the x, y and z planes, and the relative positions of dQ and dQ', it follows that:

$$z' / p' = \rho \cdot \cos.\theta / p \quad \text{and} \quad p' / p = z' / \rho \cdot \cos\theta$$

$$y' / p' = \rho \cdot \sin.\theta / p \quad \text{and} \quad p' / p = y' / \rho \cdot \sin.\theta$$

$$x' / p' = D / p \quad \text{and} \quad p' / p = x' / D$$

Since from the earlier discussion of the image charge position, $p \cdot p' = a^2$:

$$p' / p = a^2 / p^2$$

Also $p^2 = \rho^2 + D^2$

Hence $p' / p = a^2 / (\rho^2 + D^2)$

The potential at the general point P (x,y,z) is therefore given by:

$$\Phi(P) = \{s / (4\pi\varepsilon_0)\} \int_0^R \int_0^{2\pi} \{\{(D-x)^2 + (\rho \cdot \sin.\theta - y)^2 + (\rho \cdot \cos.\theta - z)^2\}^{-0.5} - (a / p)\{(x - x')^2 + (y - y')^2 + (z - z')^2\}\} \rho.d\theta.d\rho$$

On-Axis Potential

This integration is too complex for analytical solution but may be simplified by considering only points on the X-axis where z=y=0. The above equations can be used to substitute for x', y' and z'. Hence:

$$\Phi(P_x) = (s / 2\varepsilon_0) \int_0^R \{\{(D - x)^2 + \rho^2\}^{-0.5}\} - (a / p)\{(x - x')^2 + y'^2 + z'^2)\}^{-0.5}\} \rho.d\rho$$

$$\Phi(P_x) = (s / 2\varepsilon_0) \left\{ \left[\{(D - x)^2 + \rho^2\}^{0.5} \right]_0^R - I_2 \right\}$$

$$I_2 = \int_0^R (a\rho \cdot d\rho) / \{p\{(x - Da^2/p^2)^2 + \rho^2 a^4 / p^4\}^{0.5}\}$$

Expanding the denominator, substituting $p^2 = \rho^2 + D^2$ and integrating:

$$I_2 = \left[(a / x^2) \{x^2\rho^2 + (xD - a^2)^2\}^{0.5} \right]_0^R$$

After substitution and rearrangement the solution for axial potential is:

$$\Phi(P_x) = (s / 2\varepsilon_0)\left[(D - x)\{\{1 + (R / (D - x))^2\}^{0.5} - 1\}\right.$$
$$\left. - (a / x)\{D - (a^2 / x)\}\{\{1 + (R / (D - a^2 / x))^2\}^{0.5} - 1\}\right]$$

On-Axis Electric Field

The field strength is given by $E(P_x) = -\text{grad}\ \Phi(P_x)$

$$E(P_x) = -(s / 2\varepsilon_0)\left[1 - (D - x)((D - x)^2 + R^2)^{-0.5} - aD / x^2 + 2a^3/x^3 - dT/dx\right]$$

$$dT/dx = d/dx\left\{(a / x)\{(D - a^2/x)^2 + R\}^{0.5}\right\}$$

$$dT/dx = -(a / x^2)\{(D - a^2/x)^2 + R^2)\}^{0.5} + (a / x)(D - a^2/x)(a^2/x^2)\{(D - a^2/x)^2 + R^2\}^{-0.5}$$

$$dT/dx = -(a / x^2)\{(D - a^2/x)^2 + R^2\} + (a / x)(D - a^2/x)(a^2/x^2)\{(D - a^2/x)^2 + R^2\}^{-0.5}$$

The solution for axial field strength is given by:

$$E(P_x) = -(s / 2\varepsilon_0)\left[1 - (D - x)\{(D - x)^2 + R^2\}^{-0.5} - aD / x^2 + 2a^3 / x^3\right.$$
$$\left. - (a / x^2)\{(D - a^2 / x)(2a^2 / x - D) - R^2\}\{(D - a^2/x)^2 + R^2\}^{-0.5}\right]$$

The electric field therefore drops off rapidly from the electrode surface to the charged disc. As the electrode approaches the disc, the field increases monotonically until contact is made or a discharge occurs to the electrode.

Applications of Field and Potential Equations

Axial Field Equation

Maximum Surface Charge Density for Isolated Charged Disc in Air

It follows from the field equation that the field due to a charged non-conductive disc when there is no electrode or other disturbing influence present (that is, $a = 0$ and $x = D$) is given by:

$$E_x = -s / 2\varepsilon_o$$

Neglecting attenuation due to the dielectric constant of the non-conductive disc, this same field must also emanate from the other side of the disc. Since air in a uniform field has a breakdown strength of about 3 MV/m, and a permittivity of about 8.85×10^{-12} F/m, the maximum surface charge density "s" that can be supported is 5.3×10^{-5} C/m^2, or 5.3 nC/cm^2.

Use of Field Meter to Measure Surface Charge Density

If a cylindrical field meter is used to measure the field above a charged non-conductive disc it will be brought axially towards the center. The field meter head is normally equipped with a shielding annulus around the head which is designed to give roughly a uniform field, approximating at small separations to an infinite flat plate. To derive the uniform field at the meter head we let D = (d + a), where "d" is the separation. In the limit as a $\rightarrow \infty$ the field becomes:

$$E_x = -(s / \varepsilon_o) \{1 - d / (d^2 + R^2)^{0.5}\}$$

$$E_x = -(s / \varepsilon_o) \{1 - 1 / (1 + (R/d)^2)\}$$

It is observed that when a field meter is brought up to a charged plastic surface, the observed field reading does not vary in proportion to the separation, as is found for a charged metal surface. Instead, the reading stays fairly constant over large ranges of separation depending on the geometry and other grounded bodies in the vicinity. This is because the grounded field meter has a charge induced in it by the plastic surface and this depresses the potential on the plastic surface. If the disc were a metal surface, charge would flow into the area below the electrode to maintain an equipotential surface. This cannot occur with a non-conductor. In order to calibrate a field meter, it must be positioned above a large metal plate maintained at constant potential by a stabilized power supply; otherwise, capacitance effects would drop the potential everywhere on the plate.

Whenever the size of a charged non-conductive surface (as given by R) is large compared with the separation, the term $(1 - (1+(R/d)^2)$ approaches unity and the field approaches $(- s / \varepsilon_o)$. Also, if the effect of the field meter is not appreciated its reading can overestimate the surface charge density by up to a factor of two if it is assumed that $E_x = (- s / 2\varepsilon_o)$.

The field is in this case doubled relative to an isolated disc in free space, since the flux is all in the direction of the grounded body. The maximum surface charge density that can be supported prior to uniform air breakdown is halved to 2.7 nC/cm^2.

Literature sources such as [60] cite this value of 2.7 nC/cm^2 as being the maximum surface charge density for a non-conductor in air. It is seen that this is only true when all the flux emanates in a single direction through the air, for example towards a grounded plate. Another case where this would hold is for a charged spherical particle in free space, where the flux all emanates from the imaginary charge at its center.

Maximum Surface Charge Density in Presence of Spherical Electrode

The onset of discharges caused by field intensification at the spherical electrode can be estimated using the known breakdown strength of air. At the surface of the electrode on the X-axis, x=a and the field:

$$E_a = -(s/\varepsilon_o)\left[3 - (D/a) + \{(D-a)(D/a-3) + R^2/a\}\{(D-a)^2 + R^2)^{-0.5}\}\right]$$

This result was first presented by Heidelberg without derivation in a 1967 paper [61]. For example, consider a 1 cm radius electrode (a = 0.01 m) positioned 5 cm (0.05 m) above a charged non-conductive disc of large radius (R = 0.5 m). In this case D = 0.06 m and:

$$E_a = -47\,(s/\varepsilon_o)$$

For an air breakdown strength of 3-5 MV/m, the maximum charge density will be in the range 5.6 to 9.4 x 10^{-7} C/m^2 (0.056 to 0.094 nC/cm^2).

In the presence of this spherical grounded electrode the disc will support about 2% of the surface charge density relative to that with a grounded plate (uniform field) above it. Relative to a completely isolated disc in free space (uniform fields above both faces) the maximum charge density is reduced to about 1%.

Inspection of the field equation shows that the axial field decreases very rapidly with distance from the electrode surface. The drop in field corresponds to the largest energy drop as charge moves towards the electrode. Observation of brush discharges shows that the brightest part of the discharge occurs as a luminous root (stem) close to the electrode.

Axial Potential Equation

Axial Surface Potential on Charged Disc

Unlike a conductor, a charged non-conductive disc does not have an equipotential surface but instead the capacitance between the disc and grounded electrode depresses the surface potential as a function of radius across the disc. While instruments are commercially available to "measure" the surface potential of non-conductors such as belts and foils, the potential reading is not meaningful and is in fact only proportional to the surface charge density. While the instruments are calibrated in volts, the calibration is done using a metal plate held at fixed potential and there is no equivalence with the potential on a non-conductor.

The surface potential can be found by setting x = D:

$$\Phi_D = (s/\varepsilon_o)\left[(a - a^3/D^2)\{1 - RD/(D^2 - a^2))^{0.5} - 1\}\right]$$

If the surface potential is "measured" using a field meter the value will be severely underestimated relative to a metal plate of constant potential, owing to the potential depression by the induced countercharge on the grounded meter head.

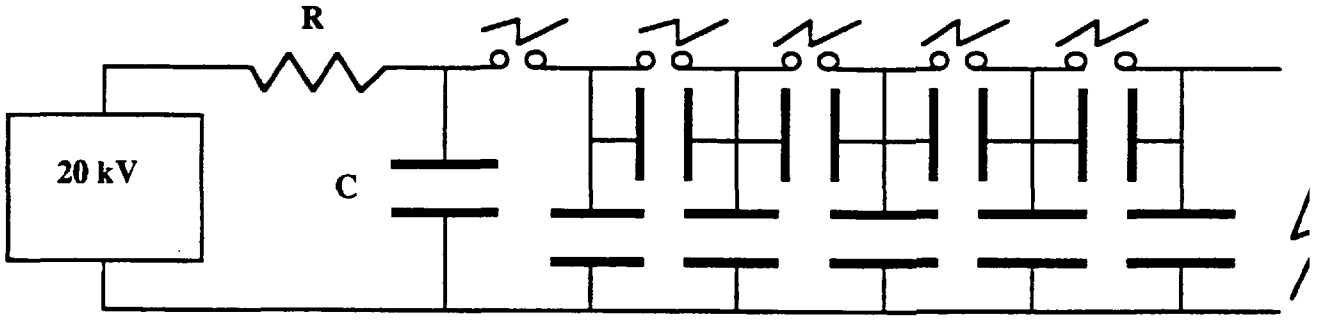
Non-Conductive Layers on Conductive Surfaces

Nuisances and hazards of non-conductive layers on conductive surfaces have arisen in many practical situations. If the non-conductor is charged on the upper surface by rubbing, by charge deposition from a flowing liquid, by particle impact, or by corona discharge, the flux due to the charge passes largely through the non-conductor to the image countercharge on the conductor underneath. The situation is analogous to a parallel plate capacitor.

If the non-conductor is very thin the capacitance with respect to the underlying conductor is very large and very large charge densities can be supported, limited only by the dielectric strength of the thickness of non-conductor involved.

The approach of an electrode, a sudden impact or continued charge deposition may trigger breakdown of the charged layer by puncture through to the metal substrate. Robb [80] illustrated the mechanism with reference to lightning stepped leaders whereby lightning propagates from cloud to ground with far less potential than would be indicated from air sparkover data. This is shown in Figure H.12, in which a capacitor charged to 20 kV (which has a normal sparking distance of about one-quarter inch) can propagate sparks over distances 50-100 times as far owing to the capacity provided along its path. This provides a very steep gradient at the stepped discharge wavefront and thereby keeps the discharge propagating. In [80], a 1 μF capacitor "C" at 20 kV discharged to give an 18 inch spark running along the outside of a series of spark gaps attached to uncharged capacitors mounted on a vertical column (note only a few capacitors and spark gaps are shown in Figure H.12). An analogous process occurs over the surface of a charged non-conductor with metal substrate, on which each surface element has a coupled capacitor on the underlying metal plus coupling with each other surface element.

Figure H.12 : Step by Step Discharge Mechanism Producing Long Discharge with Relatively Low Voltage



Maximum Stored Energies

In the absence of second conductive bodies such as electrodes approaching the charged non-conductor, the maximum stored energy can be calculated knowing the dielectric strength of the non-conductive layer of thickness "t".

The energy stored by a parallel plate capacitor holding charge "Q" on one plate is:

$$W = Q^2 / (2C)$$

Now $C = \varepsilon_o \varepsilon_r A / t$

where A = area of one plate

ε_r = dielectric constant of layer

Hence $W = Q^2 t / (2\varepsilon_o \varepsilon_r A)$

The charge Q is equal to the product of surface charge density "s" and area:

$$W = s^2 t A / (2\varepsilon_o\varepsilon_r)$$

The maximum energy occurs when the electric field through the non-conductor equals its dielectric strength. The electric field for a parallel plate capacitor is given by:

$$E = Q / (\varepsilon_o\varepsilon_r A) = s / (\varepsilon_o\varepsilon_r)$$

If the dielectric strength is written as E_d the maximum surface charge density s_{max} is:

$$s_{max} = E_d (\varepsilon_o\varepsilon_r)$$

On substitution for $s = s_{max}$ one obtains the maximum stored energy W_{max}:

$$W_{max} = t A E_d^2 \varepsilon_o\varepsilon_r / 2$$

Dielectric strengths vary with manufacture but are usually in the range 100 - 700 volts/mil (3.94 - 27.6 MV/m). Typical dielectric properties from the CRC Handbook (49th Edition) are given in Table H.1.

Flashover Considerations : Energy Released from Puncture

Robb [80] considered the case where a circular charged surface is discharged radially over some flashover radius "r" following puncture. Discharge occurs at the puncture voltage "V_p" through to the metal substrate, which is equal to the product of dielectric strength "E_d" and dielectric thickness "t":

$$V_p = E_d \cdot t \quad \text{(volts)}$$

If "V_f" is the flashover voltage per unit distance on the surface, all the surface charge within radius "r" will feed into the puncture, where this radius is given by:

$$r = V_p / V_f = E_d \cdot t / V_f$$

The discharged energy is given by:

$$W_d = C \cdot V_p^2 / 2$$

where $C = \varepsilon_o\varepsilon_r \cdot \pi \cdot r^2 / t = (\varepsilon_o\varepsilon_r \cdot \pi / t) \cdot \{E_d \cdot t / V_f\}^2$

So $W_d = \varepsilon_o \cdot \varepsilon_r \cdot \pi \cdot E_d^4 \cdot t^3 / (2 \cdot V_f^2)$

A typical surface flashover voltage [80] is 4×10^5 V/m. Using Table H.1 the energy discharged can be calculated for different cases.

Table H.1 : Typical Dielectric Properties of Solid Non-Conductors

Dielectric	ε_r	ρ	Dielectric Strength (E_d)	
		ohm-m	volts/mil	MV/m
epoxy cast resin	3.62	10^{14}-10^{15}	400	15.7
methyl methacrylate (cast/molding)	2.7-3.2	$>10^{12}$	450-500	18-20
nylon (F.M.3001)	3.5	$4x10^{12}$	470	18.5
phenol formaldehyde resin (molding)	4.5-5.0	10^{9}-10^{10}	300-400	12-16
as above with glass fiber filler	6.6	$7x10^{10}$	140-370	5.5-14.6
polyethylene	2.3	$1.6x10^{11}$	460	18.1
PTFE	2.0	$>10^{13}$	480	18.9
rubber (hard)	2.8	$2x10^{13}$	470	18.5
shellac	n/a	$1.8x10^{7}$	200-600	7.9-23.6

It is seen that the maximum energy stored per unit area is of the order Joules per square meter even for thin layers. For example, a 40 mil (~1 mm) layer of polyethylene will store 3.3 Joules of energy per square meter.

Release of this stored energy can be precipitated in several ways. A charged plane layer can discharge directly by puncturing once the dielectric strength has been exceeded. Alternatively, ionization may begin close to a boundary where field intensification is present due to a grounded body. The discharge can also occur when the layer is mechanically stressed such as by impact from a second body, which need not be a conductor. Finally, the layer can be discharged by the approach of a grounded body which causes a local discharge once the field above the layer exceeds the breakdown field of air. The local discharge can spread over most of the surface if the initial charge density is great enough to allow lateral propagation of stepped leaders to occur.

Approach of Electrode to Charged Non-Conductor with Conductive Substrate

Heidelberg [67] concluded that rigorous solution to the problem of a grounded electrode approaching charged non-conductive layers on metal substrates is complex but can be approximated by considering the isolated effects of the charged layer on the non-conductor and an equal image charge on the conductive substrate. This demands that the image charge on the electrode is small compared with that on the substrate, which should be true when the layer thickness "t" is very small compared with the distance to the electrode center "D". Now it has been shown that the axial field at the electrode surface is:

$$E_a = -(s/\varepsilon_o)\left[3 - (D/a) + \{(D-a)(D/a-3) + R^2/a\}\{(D-a)^2 + R^2)^{-0.5}\}\right]$$

The net field at the electrode can be approximated by the difference between that due to the charge array on the non-conductor "$E_a(D)$" and its image charge on the substrate "$E_a(D+t)$", where the latter charge is an additional distance "t" from the center of the electrode:

$$E_a(net) = E_a(D) - E_a(D+t)$$

If the net field is calculated in this way and it is assumed that "t" is small compared to (D-a) the net field approximates to:

$E_a(net) \sim st / (2\varepsilon_o a)$

This approximation will evidently not hold when the electrode nears the charged surface as the induced charge on the electrode will no longer be insignificant. However, it shows that electrical breakdown at relatively large separations will be determined principally by the ratio of layer thickness to electrode radius.

LITERATURE SEARCH

Keywords and Phrases

The literature search has been compiled using keywords and key phrases for cross-referencing. The literature is first compiled by source and then by subject. Keywords and phrases are given for each "source" reference except those in the "Textbooks" and "Standards" categories, which are too general to be assigned useful keywords.

Source Headings

The bibliography is subdivided into fifteen source headings. Rich sources such as "Journal of Electrostatics" and "Institute of Physics" were given special sections. Other sources were grouped rather arbitrarily depending on the ease of grouping and the number of articles found as the compilation was put together. Source headings comprise:

(A) Petroleum Institute Sources
(B) Institution of Chemical Engineers
(C) Miscellaneous Conferences
(D) Newsletters, Newspapers and Magazines
(E) Journal of Electrostatics
(F) Miscellaneous Journal Articles
(G) Electrical Engineering Symposia and Journal Articles
(H) Manufacturing Chemists Association Case Histories
(I) Institute of Physics
(J) Patents
(L) Loss Prevention (AIChE and International Symposia)
(N) Industrial, University and National Agency Reports
(P) Plant / Operations Progress
(S) Standard / Recommended Practices
(T) Textbooks and Compendium Articles

Subject Headings

The bibliography is compiled chronologically under twenty-five major subject headings:

(1) Accident Case Histories
(2) Antistatic Additives and Measures for Liquids and Plastics
(3) Aviation
(4) Bonding and Grounding
(5) Charged Fuel Mist, Spray and Froth
(6) Discharges from Charged Liquids
(7) Discharges from Plastics
(8) Drums I : Lined/Unlined Steel
(9) Drums II : Plastic
(10) Filters and Strainers : Electrification
(11) Instruments and Measurement Techniques
(12) Neutralizer Systems for Charge and Field
(13) People : Shoes, Clothing, Carpets, Floors
(14) Pipes and Hoses I : Non-Conductive or Plastic Lined : Electrification and Relaxation
(15) Pipes and Hoses II : Conductive or Metal : Electrification and Relaxation
(16) Prostatic Agents and Multiphase Systems

(17) Relaxation and Conduction Theory
(18) Steam Jets, Water Curtains, Inertion Systems, Fire Extinguishers
(19) Stray Currents
(20) Tanks I : Conductive or Plastic Lined : Charge Accumulation : Hazards : Experiments : Models
(21) Tanks II : Non-Conductive or Plastic : Charge Accumulation : Hazards : Experiments : Models
(22) Tanks III : Small Non-Conductive Containers less than 55 Gallons
(23) Valves : Ball Valves
(24) Washing and Cleaning Tanks and Tankers
(25) Powder handling : addition to solvents or handling in flammable vapor atmospheres

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Keywords: discharges from charged plastics. brush discharges. calculation of field and discharge energy.

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Keywords: discharges from plastics. propagating brush. onset conditions.

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[E.63] Finke, J., "Electrostatic Effects of Charged Steam Jets", J. Electrostatics, Vol. 23, April (1989).

Keywords: steam jets. electrification. model. field strength. brush discharges. sparks.

[E.64] Norberg, A., et al., "On the Pulse Shape of Discharge Currents", J. Electrostatics, Vol. 23, April (1989).

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Keywords: tank filling. streaming current model. computer model for tank filling. maximum permissible filling rates.

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(F) : MISCELLANEOUS JOURNAL ARTICLES

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Keywords: stray currents. RF radiation. theory. review of Standards. spark ignition experiments. behavior of industrial structures.

[F.2] Hughes, J.F., "Electrostatic Charges on Board Ships", Trans. I. Mar. E. Vol. 92, TM6 (1980).

Keywords: tank filling. tank washing. charged mist. water slug. plastic tanks. plastic pipes.

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Keywords: charged fuel mist. xylene spraying. electrification. power dependence of current on velocity, nozzle diameter and conductivity.

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Keywords: tank truck loading. petroleum products. surface potential. discharges from liquids. safe procedures. relaxation times. filters.

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Keywords: tank trucks. need for drag chains. grounding.

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Keywords: discharges from charged liquids. steel drum. filter. effect of oil polarity. discharge energy. submerged electrodes. effect of electrode geometry.

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Keywords: discharges from charged liquids. large surface discharges. general remarks on safe tank filling.

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Keywords: tank truck loading and unloading. automobile tank filling. tire resistance. measurement of streaming currents. grounding. assessment of vehicle potentials.

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Keywords: tank filling tests. filters. drop loading. electrification. passive neutralizers. SCR. antistatic additives. effect of drop tube design.

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Keywords: charge relaxation. hyperbolic theory. charge carrier mobility.

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Keywords: discharges from charged plastics. gas ignition tests. effect of electrode radius. brush discharge. effective discharge energies. charge transfers. surface charge density. effect of relative humidity.

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Keywords: discharges from charged plastics. brush discharge. effect of polarity. calculation of energy discharged.

(G) : ELECTRICAL ENGINEERING SYMPOSIA AND JOURNAL ARTICLES

[G.1] Deno, D.W., "Calculating Electrostatic Effects of Overhead Transmission Lines", Paper T 74 086-5, IEEE PES Winter Meeting, New York, N.Y., January 27-February 1 (1974).

Keywords: stray currents. overhead transmission lines. voltage gradient at ground level. induced charges on people and objects.

[G.2] Howard, J.C., "Static Electricity in the Petroleum Industry", Electrical Engineering, pp. 610-614, July (1958).

Keywords: tank truck loading. charges on free oil surface. qualitative guidelines.

[G.3] Owens, J.E., and Schorn, B.E., "Electrostatic Ignition Hazards with Flammable Liquids", IEEE Transactions on Industry Applications, Vol. IA-16, No. 6, November/December (1980).

Keywords: electrification. agitation. slurries. multiphase systems. safe charge density. effect of conductivity on charge density. safe conductivity. use of antistatic additives. small non-conductive containers.

[G.4] Deno, D.W., "Electrostatic Effect Induction Formulae", IEEE Transactions on Power Apparatus and Systems, Vol. PAS-94, No. 5, September/October (1975).

Keywords: stray currents. power transmission lines. formulae for calculating induced charge on people and objects at grade.

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Keywords: effect of liquid conductivity on charging. table of conductivities for organic chemicals. review of Nitka's conductivity approach.

[G.6] Lees, P., et al., "An Experimental and Computational Study of Electrostatic Field during the Pumping of Powder into Small Metal and Plastic Containers", IEEE Transactions on Industry Applications, Vol. IA-21, No. 5, September/October 1985.

Keywords: modeling of container filling. finite element method. use of small scale tests to help understand full scale phenomena. plastic tanks. filling with powder (method could be adapted for liquid filling).

[G.7] Asano, K., "Electrostatic Potential and Field in a Cylindrical Tank Containing Charged Liquid", Proc. IEE, Vol. 124, No. 12, (1977).

Keywords: analytical solutions for potential and field. cylindrical tank filling. steel drums.

(H) : MANUFACTURING CHEMISTS ASSOCIATION CASE HISTORIES

Note : MCA Case Histories are out of print and no longer available

[H.1] (Anon), "Static Spark Flashes 'Empty' Styrene Drum", MCA Case History No. 41, MCA Case Histories Vol. 2, January (1966).

Keywords: ungrounded drum. styrene vapor. steam cleaning. explosion.

[H.2] (Anon), "Hand Pump Generates Static", MCA Case History No. 73.

Keywords: drum. rotary hand pump. hose nozzle ungrounded by pipe dope. fire.

[H.3] (Anon), "Xylol Flash", MCA Case History No. 91.

Keywords: pebble mill. xylene addition. brush discharge on pebbles. fire.

[H.4] (Anon), "Fire Due to Static Spark : Benzene", MCA Case History No. 129.

Keywords: glass containers. benzene pouring. ungrounded funnel. fire.

[H.5] (Anon), "Vinyl Acetate Explosion and Fire : Fatality", MCA Case History No. 384.

Keywords: tank car. vinyl acetate. insulating hose. ungrounded nozzle. explosion. fatality.

[H.6] (Anon), "Fire : Carbon Disulfide", MCA Case History 558.

Keywords: pipe leak. carbon disulfide. separartion of layers of plastic and pipe insulation. ungrounded steel barrier. fire.

[H.7] (Anon), "Static Ignition", MCA Case History 610.

Keywords: grounded drum. siphoning dioxane to reactor through polyethylene tube. gauze filter wired to end of hose. spark or brush discharge. fire.

[H.8] (Anon), "Minor Explosion in Handling of Chopped Rubber", MCA Case History No. 674.

Keywords: loading chopped rubber to styrene tank. ungrounded operator. induction. spark. fire.

[H.9] (Anon), "Explosion in Vent Stack : Static Generation", MCA Case History No. 703.

Keywords: ungrounded operator. methyl alcohol and benzene vapor. spark. fire.

[H.10] (Anon), "Ignition of Toluene Vapor by Electrostatic Spark", MCA Case History No. 742. (note: analogous to case history number 610).

Keywords: vacuum transfer of toluene from drum through plastic tube. flannel filter wired to end of tube. discharge from wire during withdrawal from drum. fire.

[H.11] (Anon), "Xylene-Petroleum Naphtha Vapors Ignite while Loading Centrifuge", MCA Case History No. 748.

Keywords: loading centrifuge. xylene-petroleum naphtha vapor. brush discharge from charged cake to wash line nozzle. fire.

[H.12] (Anon), "Static Spark Fires Vapor During Drum Filling Operation", MCA Case History No. 832.

Keywords: splash filling of drum with styrene monomer. possible discharge from plastic filling pipe (unspecified). blamed on poorly grounded drum (unlikely).

[H.13] (Anon), "Static Ignites Ligroin in Centrifuge", MCA Case History No. 876.

Keywords: centrifuge basket ungrounded by grease on bearings. splash filling of slurry in flammable distillate. possible ungrounded operator. spark. fire.

[H.14] (Anon), "Static Charged Spray of Hot Toluene Ignites", MCA Case History No. 886.

Keywords: toluene recycling through filter. glass lines. plastic vent hose. plastic bucket. fire.

[H.15] (Anon), "Handling a Flammable Solvent", MCA Case History No. 939.

Keywords: tank trailer gauging with metal gauge stick. flammable solvent. possible ungrounded operator. explosion.

[H.16] (Anon), "Possible Static Electricity Flashes Flammable Vapors", MCA Case History 958.

Keywords: dumping solids from fiberpack with plastic liner to centrifuge containing flammable vapor. brush discharge from liner or spark from ungrounded operator. fire.

[H.17] (Anon), "Ethyl Acetate Tank Truck Explosion : Static Electricity", MCA Case History 986.

Keywords: tank truck loading. ethyl acetate. cloth filter. large filling rate. brush discharge from liquid surface to copper thermometer cup. fire.

[H.18] (Anon), "Explosion and Fire : Lead Azide", MCA Case History No. 987.

Keywords: ungrounded operator. non-conductive shoes. lead azide. spark. explosion. fatality.

[H.19] (Anon), "Explosion in Centrifuge", MCA Case History No. 1072.

Keywords: rubber lined centrifuge. plastic pipe. plastic lined pipe. gravity feed of slurry. methylcyclohexane and toluene solvents. explosion.

[H.20] (Anon), "Flammable Liquid Transfer Explosion", MCA Case History No. 1309.

Keywords: splash filling ungrounded drum. explosion.

[H.21] (Anon), "Methanol Vapor: Static Spark: Explosion", MCA Case History No. 1443.

Keywords: methanol transfer from drum to makeshift funnel in plastic pipe. spark from funnel or ungrounded operator. fire.

[H.22] (Anon), "Centrifuge Explosion", MCA Case History No. 1478.

Keywords: lined centrifuge. methyl ethyl ketone vapor. drop filling of slurry. explosion.

[H.23] (Anon), "Flash Fire", MCA Case History No. 1479.

Keywords: wiped Teflon rod. inserted into glass lined crystallizer containing ethanol vapor. brush discharge. fire.

[H.24] (Anon), "Static Electricity Fires Casting Powder", MCA Case History 1517.

Keywords: solvent-wet propellant powder. pouring. non-conductive shoes. fire.

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Keywords: review. models for streaming current. contaminants. non-conductive pipes. relaxation. spray electrification. tank cleaning. discharges from charged mist. antistatic additives. neutralizers.

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Keywords: electrification in pipes and filters. mechanism. relaxation. conductivity.

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Keywords: tank and tanker washing. tank field strength. charged mist. accident histories.

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Keywords: tank and tanker washing. charged mist. analytical models for potential and field.

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Keywords: tank and tanker washing. charged mist. electrification mechanism. effects of conductivity and jet velocity on charging.

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Keywords: test methods for textile charging. resistivity. antistatic materials.

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Keywords: antistatic clothing. test methods. resistivity criterion. coated fabrics. gas ignition tests. discharges from people. body voltage.

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Keywords: road and rail tank car filling. experimental tests. streaming current. charging in filter. discharges from charged liquid. spark energy estimates. gas ignition tests. use of antistatic additives. effect of splash filling. effect of dip pipe length.

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