THE OIL TANKER AND THE CHARGED MIST

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It is shown that a charged mist produced by splashing during tank washing operations may easily produce an incendiary discharge under conditions that can be clearly specified. However, there is no clear understanding as to the manner in which the charged mist may interact with various objects, including the water jet, to produce these hazardous conditions. Since the amount of electrical energy required to produce an ignition is always exceeded by the electrical energy available in the mist, a summary is provided describing how the mist obtains its charge and how it behaves mechanically and electrically. It is shown that the behavior observed with detergents is exactly as expected, and it is suggested that chemicals be properly evaluated as a possible solution for the prevention of the generation of charge, which will also provide information regarding previous accidents. It is shown that the aerodynamic flow induced in a tank during washing is sufficiently turbulent to guarantee the effectiveness of measuring equipment in evaluating overall mist properties. This is because the charged particles in the mist are in a range of charge and size that does not allow them to have any significant electrically induced motion of their own; consequently, they follow the turbulent gas motion and are rapidly uniformly mixed throughout the tank, except possibly very near the walls at the region of splashing. It is shown that ions produced by corona discharges at the wall of the tank provide an effective sink of charge that is related to tank size effects, is responsible for the equilibrium charge density and maximum potentials, and prevents the formation of lightning-like discharges. The evaluation of electrical discharges in relation to their ability to ignite hydrocarbon-air mixtures at normal conditions discloses that the only corona discharges capable of producing a flame of the critical size cannot happen in a tanker. In fact, the only possible source of ignition must be a spark discharge between two electrodes that are not necessarily metal electrodes. This narrows the possibilities for an explosion to a much smaller set of candidates in which a falling body is the most likely hazard. Finally, four different avenues of approach for a practical solution are suggested.

Introduction

Approximately two years ago three new oil tanker ships, the pride of their owners and operators, exploded within a one-month period. It was soon established that the tanks of all three tankers were being washed at the time of the accidents; therefore, their tanks were filled with a water mist produced by powerful cleaning jets of water. The possibility arose that these mists could be electrically charged. Consequently, the possibility of producing an incendiary electrical discharge associated with the charged mist became a suspect and, hence, the subject of intensive study. Although no definite explanation has been found for the three catastrophes, it has been established that an inherent electrical hazard associated with the mist produced during washing does exist.

From a technical point of view, the three tanker accidents focused a spotlight on a very old problem that has never been properly understood, namely, the manner in which either solid or liquid dispersed matter accumulates charge, and how it may release this charge through an electrical discharge when the accumulation becomes very large. The problem is difficult to study because it involves very rapid events associated with either very large volumes or transient accumulations of charge that disappear very rapidly due to mutual repulsion of the charged particles. However, the effect does cause problems in other areas, and when it does, it does so also in a gradiose way, i.e., explosions in coal mines or flour mills and, of course, damage produced by lightning. Within the oil industry, intensive surveying has disclosed that unexplained fires on tankers or OBO ships are not rare, and the possibility of ignitions associated with electrical phenomena cannot always be excluded. For instance, the author was surprised to learn that the S.S. V.A. FOGG went down together with 39 persons due to an explosion produced while tanks, previously filled with benzene, were being washed without any precaution regarding the possibility of an electrostatic hazard. Of course, there is no way to insure that the explosion was triggered by an electric discharge, but, definitely, the probability of such an explosion was higher because of the lack of concern about electrostatic hazard.

This report constitutes an effort to communicate some of the technical background and also the results of many recent studies carried out both at this university and at the research laboratories of several oil companies. Only the possibility of an explanation due to electrostatic causes is considered. Also, no attempt is made to go into a detailed description or evaluation of each technical result, but, rather, an effort is made to incorporate its significance into what is hoped to be an easily readable summary of the involvement of electrostatics in the tanker explosion problem.

The Typical Charged Mist in a Tanker

It is an experimental fact that inherent in the use of cleaning equipment incorporating jets of water is the production of a charged mist capable of producing electrical discharges in the tank being washed (See API Reports, 1970, 1971, and unpublished reports, References Section). The resultant mist is positively charged when using sea water but becomes negative when DASIC (trade name of a detergent) is used above a certain concentration. Using portable washing machines, it is observed that the charge density is, in general, smaller in a larger tank, but no difference can be obtained regarding the number of portable machines in the same tank. The fact that the space variation of the charge density is always measured to be negligibly small is very important. After washing, the charge decay and visual disappearance of the mist take hours but can be reduced to a fraction of an hour using air blowers.

It has been shown that these observations indicate charging of the mist produced by the disruption of water surfaces, which accompanies splashing of the water at the wall being cleaned. The resulting charged particles inside the tank away from the region of splashing exhibit negligible electrostatic dispersion. That is, due to their characteristic size, they are strongly influenced by aerodynamic and gravitational forces; if the mist moves, charged particles move with the gas, and some of them are heavy enough to fall through the mist. However, in contrast to molecular ions, the resulting charged particles can only move very slowly due to electrical forces alone. Also, since the measured charge density is not dependent on position in the tank, it is established experimentally that the washing machines generate enough turbulence to maintain the charged mist completely stirred and well mixed throughout the tank. At equilibrium (no change with time), the charge generation mechanism must be counterbalanced by processes that destroy charge per unit time in exactly the same amount that it is produced. These sink processes seem to be dependent on overall properties of the resulting mist and not directly on phenomena associated with its local rate of generation or with local inhomogeneities. In other words, the electrical parameters characterizing the mist have equilibrium values limited by induced physical processes that are switched on, or enhanced, to become effective at predetermined values of the extensive properties of the mist. These are properties that are basically additive, such as charge, mist-filled volume, tank size, electric field, particle radius, etc. Sink processes are, for instance, gas ionization, particle coagulation, charge recombination, diffusion to the walls, etc. The point is that, due to the homogeneity of the mist, it is, in principle, always possible to identify sink processes that determine an equilibrium level. Moreover, this level is characterized by measurable properties of the mist; therefore, if one of the switched-on or enhanced phenomena is undesirable, it is possible to know when it is going to occur in order to avoid it.

Formation of the Charged Mist

The process of charge generation by the breakup of water surfaces has been studied intensely regarding splashing, spraying and bubble bursting phenomena. In addition to industrial, product-oriented studies, the primary motivation has been thunderstorm electrification and the production of atmospheric condensation nuclei. (These are very small particles that act as centers where water vapor condenses. They are required for the formation of natural clouds.) The basic work is very nicely reviewed in publications by Loeb (1958) and Blanchard (1963). More recent developments have been published by Workman (1967), Iribarne et al. (1967, 1970 a,b) and Shewchuk and Iribarne (1970, 1971). The separation of charge when a water surface is disrupted is a basic property of water associated with its chemical structure. Electrically, water molecules behave as small rods each with a positive and a negative end, that is, as permanent dipoles. Inside the bulk material and in the absence of an imposed external electric field, these dipoles are always randomly oriented due to thermal agitation. There are about 3×10^{22} such molecules per cubic centimeter. Of these, about 10^{13} dissociate into separate positive H^+ and negative OH^- ions that are also in constant random agitation and are responsible for the conductivity of pure water. At the air-water interface, there are 10^{15} H_2O dipolar molecules per square centimeter. These are not as greatly affected by random agitation as the bulk molecules. It is estimated that one out of every 30 molecules is selectively located perpendicular to the interface with its positive side sticking into the water. Dipoles have no net charge, but their organized alignment causes negative ions, in the bulk, to be attracted into the surface. These negatives, in turn, attract positive ions. However, these positive ions are already deep enough into the bulk water to be affected by thermal random agitation. Consequently, their attraction to the surface is not as strong as that between the surface-oriented dipoles and negative ions. As a result, there is an average net negative charge right next to the air-water interface. It is estimated that there is one net negative ion for each 10^4 to 10^5 water molecules in a surface layer of the order of 8×10^{-7} cm thick. The positive ions are about 10^{-6} cm below the surface.

In a rapid process of water surface separation, such as splashing or spraying, very thin filaments and films are produced involving sizes of the order of the charge layers in an undisturbed surface. From the picture presented in the previous paragraph, it is clear that such violent processes are accompanied by the establishment of strong electrical forces and flow of charge that will finally result into droplets with net charge of both signs. Since there are more negative ions close to the surface, one would expect a small excess of negatively charged droplets among the smaller droplets, and, conversely, a small excess of positive droplets among the larger drops that are big enough to fall, thus leaving a net negative mist. This is, in fact, observed. The total amount of positive or negative charge separated per gram of splashed or bubbled water is around 7×10^{-9} coulombs. The excess negative charge among the small particles is approximately 6×10^{-10} coulombs per gram of splashed water. The average size among the smaller positive and negative particles is of the order of 10^{-6} cm in diameter. These are too small to fall, being suspended by Brownian thermal motion. Nevertheless, they can only move in still air at a velocity around 5 cm/sec under the influence of the largest field values measured in tankers (10^2 kv/m or 10^3 v/cm). This speed is smaller than that generated by turbulence produced by the washing machines; hence, it is not surprising to have a well-mixed mist. (Based on the operating conditions of a Super-K machine, it is estimated that the velocity of the particles near the wall is around 10^2 cm/sec). It is noted, however, that for every net charged droplet there should be around 11 particles, both positive and negative. It will be shown later that all these small particles are short lived; however, in the mist the presence of many charged droplets with no net charge is to be expected and may play a role in both stability and decay of the net charged cloud.

The main discrepancy between the simplified theory just presented and the results of tanker washing using sea water and clean tanks is that, as indicated, the net charge in tankers is positive, opposite to that predicted and observed using pure water. The effect is not unexpected and has been studied using different chemicals in solution with the water. Salt solutions are known to enhance the electrification of water and at higher concentrations reverse the excess difference between positive and negative drops, thus producing a net positive mist. From the picture presented it is clear that anything affecting surface properties will also affect the charge separation mechanism. The effect of salt is not only electrolytic, i.e., associated with salt ions in solution, but, more important, is the change and increase in surface tension because this discourages the formation of very thin films and filaments. Although the average final size among the small droplets remains about the same, the enhanced charging is more symmetric, and the difference between negatives and positives becomes smaller. The reason why a concentrated solution reverses the net charge is not clear cut. It involves relationships between electrical and mechanical relaxation times, as well as the effect on surface properties produced by both electrolytic ions in solution and undissociated salt molecules. In addition, the velocity of the water at the point of splashing, as well as the quality and material of the surface being hit, also affect the charging mechanism. Again, the point is that the observed experimental changes using sea water, oil water mixtures and DASIC are not unexpected. They are all closely related to the condition of the wall and the water surface at the time of splashing and bubbling activity produced by the impact of the cleaning jet on the wall of the tank.

Mechanical Properties of the Charged Mist

The measurement of charge density in a tank indicates complete mixing at the time of measurement. It does not provide any information regarding the time required for turbulent motion to remove charged droplets from a region near the wall or the time required to mix charged particles, homogeneously, in the bulk of the tank. Also, it is clear that turbulence will carry not only the very small particles responsible for most of the net charging, but also any charged or uncharged droplet able to move along with the gas (air). Clearly, the mist produced near the wall incorporates a wide range of sizes, and in order to determine the behavior of such polydispersed aerosol some basic concepts must be considered. (Detailed information can be obtained from standard textbooks, such as, Fletcher (1962), Fuchs (1964), Green and Lane (1964), and Mason (1971).

In addition to motion induced by a moving gas carrier, an aerosol droplet experiences motion due to impacts with gas molecules, characterized by the temperature (Brownian motion), and a settling motion due to its mass and characterized by gravitational attraction. Which one of these two effects predominates depends, of course, on particle size that is completely determined by droplet radius in the case of a liquid aerosol. Fortunately, the region where the two effects may both significantly contribute to the motion of the drop is quite narrow. In general, small particles are governed by different considerations than larger drops. For example, under normal temperature and pressure, a particle with a radius of 10^{-4} cm moves in one second under the influence of molecular impacts only 3 percent of the distance due to settling effects (1.28×10^{-2} cm/sec). Conversely, a particle ten times smaller ($r = 10^{-5}$ cm) moves in one second under the influence of molecular impacts, a distance that is 7.5 times the distance computed for settling effects (2.24×10^{-4} cm/sec). In other words, for particles larger than 10^{-4} cm, thermal impact effects are negligible, and for particles smaller than 10^{-5} cm, there is no contribution due to the gravitational settling motion of the particles.

In order to obtain some indication of the mixing speed characteristic of the gas motion in a tank, a charged sample, opposite in polarity to the net charge in the mist, was introduced at one end of a center tank while it was being washed (S.S. PEGASUS). The time required for this charge to reach the opposite side of the tank was monitored, and it was calculated that the sample charge moved at an average speed of 20 cm/sec across the length of the tank. This value will be taken as that characteristic for the aerodynamic turbulent mixing of the aerosol. As indicated, this value is significantly larger than the maximum electrically induced velocity of the smaller charged droplets ($r \approx 10^{-6}$ cm). It is also much larger than the induced random velocity for all small particles that are affected by Brownian motion. It can be concluded that all the charged and uncharged particles affected by thermal impacts are carried by the gas. They move randomly in the gas but will not fall or have any net motion except the gas motion. The larger airborne droplets have a net motion dependent on the difference of velocities produced by settling, gas viscosity and electrical forces. The latter will be considered later and shown to be negligible; therefore, it is concluded that the mist can only carry particles with a settling velocity that is small compared to the average turbulent speed. Big particles with velocities larger than the mixing speed of 20 cm/sec can be expected to be present only as transient particles in their way from the region of production to the bottom of the tank. 20 cm/sec corresponds to the terminal settling velocity of particles 4.3×10^{-3} cm in radius. Particles 10 times larger fall from the top to the bottom of a large tank (80 feet) in about 15 sec. This is a short time compared to the times observed regarding stability and mixing of the cloud (at least several minutes). It may be safely concluded that the turbulent mist can only hold particles in a range determined at one extreme by the smaller particles produced by splashing ($r = 10^{-6}$ cm) and at the other by the largest particles able to be carried by turbulent motion ($r \approx 5 \times 10^{-3}$ cm). The range of possible sizes for particles in the stable mist ($10^{-6} < r < 5 \times 10^{-3}$ cm) is, however, quite large, and the life of any particle, particularly the small ones, is strongly affected by time and overall concentration of particles.

Interaction between small and large, but airborne, particles is strongly dependent on thermal motion of the small particles. This is as expected because these particles are able to move rapidly among the larger ones with which they collide and coalesce. The process is treated as thermal coagulation theory. Consider first an isodispersed aerosol where all particles are identical with a radius, r, and a concentration, n per cubic centimeter. Coagulation theory considers the diffusion of particles into a stationary test particle. Each particle is then considered a test particle, and it is assumed, and verified experimentally, that every collision results in coalescence. The decrease in concentration with time is then obtained in terms of the initial number of particles per unit volume, n_o, and a constant, k, characteristic of the aerosol, and referred to as the coagulation constant.

$$\frac{1}{n} - \frac{1}{n_o} = kt$$

The main property of this equation is that, when a coagulation process does take place, it may be identified from experimental data because a plot of the inverse of the concentration versus time is a straight line with slope k. The coagulation constant determines how fast the concentration decreases and turns out to be a function of viscosity, temperature, and particle size. For a fixed gas, droplet substance and temperature, k is only a function of particle size. However, the variation of k with particle size depends on the size considered. It changes by a factor of 4 as r changes by a factor of 100 from 10^{-7} to 10^{-5} cm. It has a maximum value at 10^{-6} cm ($k = 1.2 \times 10^{-9}$ cm^3/sec), but from 10^{-6} cm to 10^{-4} cm, it decreases slowly. For particles greater than 10^{-4} cm, thermal coagulation in an isodispersed system does not mean very much because, as indicated, the size is large enough for settling motion to overcome random motion. The very small overall change of k with size of the droplets provides evidence that, as the particles grow slower and heavier, the reduction in collision and coalescence ability is counterbalanced by an increase in size and collision cross section. The values of k make it evident that very highly concentrated aerosols are extremely short lived. For instance, an initial concentration of 10^{11} cm^{-3} goes down to half this value in 0.02 sec, while a concentration of 10^6 cm^{-3} requires 30 minutes. In fact, after a few minutes, it makes no difference what the original concentration is for a highly concentrated aerosol.

Thus far no polydispersity, turbulent mixing, or charge effect has been considered regarding the stability of the particles in the mist. Polydispersity guarantees that the small rapidly moving particles will be collected by the large slow droplets. The effect is described as a change in the coagulation constant that becomes a function of the ratio of the size of the large and small particle considered. The increase in coagulation constant between the smaller and larger drops that are possible in the mist ($10^{-6} < r < 10^{-3}$ cm) is quite large, being about 8,500 times the value for an isodispersed aerosol. Turbulence increases coagulation rates further by a factor that depends on particle size and changes in the gas velocity involved. It is meaningless to assign a number describing the effect of turbulence in coagulation for a tank that is being washed. It is only fair to say that the coagulation rate is significantly increased near the walls where the small particles originate.

The effect of charge per particle in thermal coagulation depends on the ratio of electrical to thermal energy between the charged particles concerned. It may become important when only one polarity, highly charged particles are concerned, but, when both polarities are present, the combined effect is negligible. However, under any circumstances, the electrical contribution to thermal coagulation is overwhelmed by Brownian motion for the small charged particles and by turbulence for larger particles that are not very highly charged. It is necessary now to consider the possibility of very highly charged droplets. As indicated, the main contribution to net charge in the mist is by the breakup of very thin films of water. However, in a splashing process there is also the production of many larger droplets capable of being carried away with the turbulent flow ($r \leq 5 \times 10^{-3}$ cm). The amount of charge one of these droplets may carry is proportional to the square of its radius; therefore, unlike the smaller particles, these may carry many elementary charges. Particles in this range have been carefully studied by Chapman (1934), who finds that the charging produced by splashing and spraying is very accurately symmetric with no net overall charge. Individually these droplets exhibit up to 600 elementary charges for droplets 5×10^{-4} cm in radius. Their maximum electrically induced velocity will be that produced by the maximum electric field (10^3 v/cm) and limited by air viscosity. It can be easily shown that such velocity is given by (4.6×10^{-7} cm^2/sec) (N/r), where N is the number of elementary charges in the drop, and r is the radius. It follows that the maximum velocity for the highest charged droplets produced by splashing and spraying is of the order of 0.55 cm/sec, which is considerably smaller than the average turbulent speed of 20 cm/sec. It is clear, then, that all airborne charged droplets produced by splashing can be carried by the turbulent flow.

There are two more sources of very highly charged droplets that must be considered regarding electrically induced motion. One is bubbling, and the other is charging by molecular ions of the neutral or slightly charged drops.

Blanchard (1963) has shown that, in the absence of an electric field, charged droplets with as many as 10^4 elementary charges can be produced. The amount of charge and polarity of the drop depends on the size, salinity of the water and elapsed time from the moment the bubble is formed to the moment it ruptures the surface of the water. Optimum charged droplets with 10^4 elementary charges have a diameter of 2.5×10^{-3} cm, therefore, a maximum electrically induced velocity of 1.84 cm/sec. This value is still small to compete with turbulence. When the bubbles are produced in a region with a moderately strong electric field (300 v/cm = 30 kv/m using sea water), droplets are produced with a maximum of 10^6 elementary charges at 5×10^{-3} cm in radius. Even if the higher measured field (10^3 v/cm) does not enhance charging, it implies induced velocities around 10^2 cm/sec. Furthermore, the charge is net charge because the opposite polarity stays in the water from which the bubble emerges. (In a washing process and in the absence of stripping, the bottom of the tank is a much more prolific source of bubbles than the walls. Also, in a partially ballasted OBO ship, when water falls on water, bubbling is prolific).

It has been established that electrical discharges of the corona type are always present during washing. These, as will be shown in detail, are by themselves harmless, but they provide strong sources of molecular ions that, because of their extremely small size, are definitely capable of moving much faster than any droplet in the tank. A droplet located near a corona discharge finds itself in a region of high monopolar conductivity. The ambient field polarizes the drop, and ions are attracted into it until the net acquired charge stops the current flow. The charge acquired depends on the square of the radius of the drop and the ambient electric field (Gunn, 1956). Assuming the driving field is the maximum measured electric field, the velocity of a drop charged in this manner can be calculated to be $(10^4/\text{sec})\ r$. It follows that drops with a radius of 5×10^{-3} cm may obtain sufficient charge to be projected into the mist at a velocity larger than the average turbulent value.

Except as a charge sink, it is believed that the highly charged particles capable of moving effectively by electrical forces and produced either by bubbling or ion charging are not significant for the equilibrium charge and size distribution of the stable mist that is produced and maintained during washing. The reasons can be listed as follows:

A. They are produced only when a high field is already established.

B. They are most certainly significantly outnumbered by smaller charged droplets of both polarities.

C. When produced, they have polarity opposite to the net charge of the mist. They are then projected into a mist with many oppositely charged particles in the thermal range. It is believed they will rapidly lose their very high charge and, consequently, their ability to move independently of turbulent motion.

Based on coagulation theory, considering polydispersity and turbulence, it is clear that very small and very large particles produced by splashing do not contribute to the size distribution in the equilibrium stable charged mist that fills the bulk of the tank being washed. Among the sizes possible there is strong discrimination to exclude the smaller droplets, and it may be concluded that the size spectra will only have particles between 10^{-5} and 5×10^{-3} cm in radius. Some of the larger droplets may obtain very high charges due to either ion diffusion or bubbling, but these very highly charged droplets are few in number, unstable, and are not capable of altering the size or charge spectrum in the stable turbulent mist. Since induced corona discharges are present at equilibrium, and since they produce many ions of polarity opposite to the net polarity of the mist, it is clear that these ions constitute one of the required sink processes. However, it has been shown that the effect of induced coronas in a mist is not that of directly neutralizing net charge by ion-droplet interaction. Instead, droplets near the discharge are charged oppositely in polarity to the net charge in the mist and then carried away by turbulence into the bulk of the tank. The sink process is a volume effect with droplet-droplet interaction aided by turbulence. Although a mixture of positive and negative charge carriers has not been established experimentally, both the charging and sink processes considered here suggest strongly their presence.

Electrical Properties of the Mist

A net charged mist is not an electrically stable system because of the mutual repulsion of its components. It requires forces that are not electrical in nature to maintain equilibrium. In the tank these forces are provided by droplet-gas viscous interaction and, as indicated, by turbulent mixing that insures an average constant space charge density. From the electrical point of view, the equilibrium net charge may be considered, at a given time, as a fixed assembly of space charges that are held together by mechanical forces. Assume for the moment that the tank is a simple metal sphere and that the fixed charges are all positive. Consider a positive test charge that is mechanically pushed from the wall into the mist. At the wall the test charge experiences a strong repulsive force that diminishes as it moves into the tank. The total amount of mechanical work done and required to push the test particle into the mist increases continually as the particle goes into the mist. This work is stored in the system as available electrical energy. If the test particle is to be left alone, it is expelled from the assembly with an electrical force that increases as it moves away from the center. However, the amount of electrical energy available to push out the test particle is maximum at the center and decreases as one moves toward the wall of the tank. (Note that the charge assembly has stored electrical energy that equals the mechanical work that is required to bring it together.) At any given location the mechanical force required to keep the test particle stationary divided by its charge represents the electric field at the point. Moreover, the amount of mechanical work required to bring the test particle to the point in question, divided by its charge, represents the electrical potential of the point. The electric field, E (force/charge or volts/cm), is then a maximum at the walls of the tank and zero at the exact center of the tank. (The zero condition is, of course, practically unrealistic, since it holds only at one point in space.) Conversely, the electric potential, ϕ (work done/charge or volts), is maximum at the center and minimum at the walls of the sphere filled with a homogeneous charge density, ρ. Mathematically,

$$E = \frac{1}{3\varepsilon} \rho x; \quad \phi = \frac{1}{6\varepsilon} \rho \, (R^2 - x^2)$$

where ε is a constant characteristic of the medium (specific inductive capacity), x is the distance from the center of the sphere to the point in question, and R is its radius. Note that, as far as size effects are concerned, the maximum stored electrical energy is proportional to the square of the radius of the sphere, and the maximum field occurs at the wall (x=R) with a magnitude proportional to the size (R). Both values are proportional to the charge density (ρ) in the tank. For a fixed charge density the larger the tank, the stronger the electrical forces at the wall, and the higher the potential at the center. Whenever there is a difference in potential, there exists an electric field that is proportional to both the energy difference and distance between the points in question. In fact, the rate of change of potential with distance is exactly the mathematical definition of an electric field ($E=-\nabla\phi$). In a conductor there are innumerable free charges that are unable to leave the metal but are always available and capable of moving freely over its surface. This implies there can be no differences in potential, hence no electric fields, along any metal surface because free charges move within an incredibly short time (10^{-18} sec) to neutralize any net force. Note, however, that in order to counterbalance outside imposed electric fields, there may be on the surface of the metal large isotropic or isolated accumulations of "image" net charge. This charge may produce strong electrical fields (forces/charge) that are always outside and perpendicular to the surface of the conductor. For instance, at the inner surface of the sphere filled with a homogeneous positive charge density there accumulates an isotropic negative charge that is responsible for the high field near the wall. On the other hand, when a metal rod electrically connected to the wall (sounding rod, field mill, hose) is introduced into the positive mist it accumulates net negative charge on its surface that is not isotropic and increases locally in magnitude towards the center of the tank. At any point, the local accumulation is exactly the amount required to maintain the surface at the potential of the wall (zero). The accumulation of negative charge is particularly strong at the tip of the rod. The introduction of the rod into the mist implies a new field and potential distribution for the whole space, particularly for regions near the rod and at its tip. This distribution cannot be solved analytically. However, it is clear that an electric field is established from the surface of the rod at zero potential to the outside mist at the potential of the region. The electric field at the tip of the rod is the highest. It depends both on the distance to the wall and the area of the metal surface that is available for the <u>required</u> amount of negative charge to accumulate. Small areas produce higher fields at the same location, and the same area produces a higher field lower into the mist with a maximum at the center. The field at the tip of the rod is <u>always</u> <u>higher</u> and <u>never</u> characteristic of the field at the same point but without the rod. Assuming a small disturbance in the properties of the charged mist, a field reading at the tip of the rod is, at most, indicative (after calibration of the rod) of the outside potential of a region near its tip. Voltage profiles obtained in this manner do exhibit the expected variation both in tankers and shore facilities.

Any electrostatically induced explosion hazard will necessarily start as ionization by collision. This is in turn started by electrons acted upon by a threshold electric field over a minimum distance. It is, therefore, important to know where in a tank to expect high field intensities. In addition to charge density, two components, practically independent, have been identified that contribute to higher local fields: one is the actual size of the tank, and the other is the possibility of objects protruding into the mist. Of course, an actual tank is not a sphere, but the field at the wall as computed by a spherical approximation is accurate within an order of magnitude compared to the values obtained for other shapes. For instance, the value at the surface of the sphere (maximum field in the absence of protrusions) is intensified 1.5 times when considering instead of a sphere an infinitely long cylinder of the same radius. It goes up by a factor of 1.33 at the middle of the side wall in a cube that encloses the same volume as the sphere. It is three times the value at the surface of two infinitely large parallel plates that are separated a distance equal to the diameter of the sphere. That is to say, concerning the size and overall shape effects in a tank, only a limited volume of space charge contributes to the maximum electric field at the wall.

For any shape of tank, the value computed, assuming an inscribed sphere, constitutes a lower limit to the actual field value, which is, at most, three times this lower limit.

It is difficult to specify which measurement of electric field or potential, obtained in a tanker, is representative and adequate to be used in an analytical model for a space distribution in the whole tank. As indicated, the overall shape and total volume of the tank are not critical. However, there are bulkheads and supporting structures throughout the whole tank, each of which constitutes either a protruding object or an electrical wall that separates the tank into smaller volumes of effective space charge. For instance, one of the center tanks in a 200,000 DWT ship (S.S. PEGASUS) incorporates a very large bulkhead in its center. This has holes big enough to allow cargo oil, gas and mist to move freely across the tank. However, this metal bulkhead covers enough cross-sectional area to constitute an electrical barrier that isolates the aft and forward sections of the tank when considering, for instance, the effective volume of space charge responsible for the field measured near the deck. In the same tank structural members protrude about ten feet into the mist and are separated by a distance not large enough so that their effect on readings taken at the wall can be neglected. That is to say, the protruding structures locally intensify the field, but at the same time, they lower (shield) the field intensity at the surface of the wall. Thus, the value measured at the wall also becomes meaningless as a typical surface reading representative of most of the mist.

It is possible, nevertheless, to compare experimental and theoretical values based on the fact that the space charge is constant, and this has been done both in shore tests and in oil tankers. In shore facilities there are no large structural members; therefore, at any time the field at the wall and the charge density should be related only by a predictable constant. This has been verified. On a tanker, field readings are taken by placing the surface of the field meter at the same level as the structural protruding members in the tank. These readings are then compared to the values computed based on independently measured charge densities and the corresponding calculated potential of the region where the meter is located. Table I shows the results obtained by picking eight random points from data taken in three separate tests in the same tank.

Except for one number, there is agreement between predicted and observed values within 50 percent. As expected, the computed values are always smaller. Also, it must be noted that the agreement is adequate even though the charge density varies by more than a factor of six. The result is, doubtless, "too good to be true"; it does indicate, nevertheless, that the approximations made are appropriate to predict directions of change for the parameters involved and rough figures for their numerical values. It can be concluded that, indeed, the

TABLE I

Data: S.S. PEGASUS, November 1971
Tank: 4 Center; typical radius 40 feet (12.2m)
Readings: Chevron meter 10 feet below deck
Esso charge density meter 3 feet below deck.
All readings during washing.

Test No	Time	Charge Density ($x10^{-10}$ coul/m^3)	Field Intensity ($x10^{+3}$ volt/m) Predicted*	Measured	Ratio
15	0:15	46	37.2	52	1.40
15	0:55	-150	-121.0	-140	1.15
15	1:14	-155	-125.0	-135	1.08
12a	0:10	40	32.2	48	1.49
12b	2:50	-119	- 96.5	-167	1.73
9	0:50	25	20.2	26	1.28
9	1:40	36	29.1	38	1.30
9	2:00	36	29.1	42	1.44

FWD

2	13	1
4	14	3
6	15	5
- - -	- - -	- - -
8	16	7
10	17	9
12	18	11

AFT

Test 9: 6 S-K 25 ft down, holes 9,10,11,12, 17 and 18; $94 < T < 116$°F; E hole 14; ρ hole 15.

Test 12: Lav-Jet 6 ft down at hole 8; 12a no DASIC; 12b DASIC; $112 < T < 150$°F: E hole 14; ρ hole 16.

Test 15: Lav-Jet; DASIC; $78 < T < 80$°F; E hole 14; ρ hole 15.

*It is assumed that the characteristic potential of the region is reached two diameters away from the surface of the cylindrical field meter.

the manner in which this is accomplished is the critical problem that determines the possibility for any electrostatically induced process to ignite the hydrocarbon mixture in the tank considered. (The standard reference for all phases of electrical breakdown is Loeb, 1955. Corona discharges are covered extensively in Loeb, 1965. Other excellent textbooks include Cobine, 1958; Meek and Craggs, 1953; Raether, 1964, and the Encyclopedia of Physics, Volumes XXI and XXII.)

Consider first the situation where the electric field is above the critical threshold value over a small distance due to the local, induced concentration of charge at the tip of a pointed object that protrudes into the mist. If the mist is positive, the induced charge at the metal surface is negative, and the electrons in the avalanches are expelled from the region of concentrated field intensity near the metal tip. In air the avalanche electrons are produced primarily by ionization of N_2 molecules. As the avalanche progresses, the electrons move not only into a region of decreasing field intensity, but also into a region where oxygen and other electronegative molecules effectively collect them. Once collected, electrons are not only unable to produce further ionization, but they become negative ions that are able to move only as fast as the positive ions left behind them in the high field region. In actual practice, what happens is that a dipolar space charge distribution is established all around the region where the field is originally high enough to ionize the air. This dipolar space charge opposes the field concentration effect and lowers the high field near the surface of the metal to a value below that required for ionization by collision. Consequently, ionization stops and can only resume when the inhibiting space charge is disbanded by action of the existing electric field. This roughly describes the onset of a negative corona discharge in the presence of even very low percentages of electronegative molecules. The pulses are known as Trichel pulses, and in air at atmospheric pressure they start at a frequency of about 10^3 cycles/sec. Their frequency depends on the time required for the dispersal of the inhibiting ionic space charge, and this time in turn depends on the electric force acting on the negative ions away from the enhanced field region. In a metal two-electrode system consisting of a small point facing a metal plane, the time required to renew the discharge can be reduced by increasing the applied high voltage. The frequency of the pulses may then reach extremely high values (around 10^6 cycles/sec). Typical Trichel pulses produced at onset with a sharp point (0.02 cm in radius) have a rise time of 10^{-8} sec, last for almost 1.5×10^{-8} sec, and die in 3×10^{-8} sec. Each pulse produces of the order of 2×10^9 negative ions.

Consider now the situation where a negative mist fills the tank. The induced concentrated high field is due to positive charges, and there is onset of a positive corona discharge. The avalanche electrons now move in the opposite electric forces in the tank are dependent on both size (radius) and charge density (generation mechanism), but the concentration of the electric field at any protrusion into the tank most definitely determines the highest field region. The magnitude of this concentrated field is highest at the tip of the protruding grounded object and depends both on the distance from the wall and the radius of curvature of the tip. If stable, the field concentration effect becomes very small only a few radii away from the surface of the tip. The actual distance over which the field is locally intensified can be large or small depending on the radius of curvature of the tip. In general, because of the surface area effect, the stronger fields are produced by sharp points but extend only for the small distance, which corresponds to a few radii when considering the sharp point.

The electrical equilibrium condition just described is based on a detailed complicated balance between electrical and mechanical forces. This balance is possible only because of the very slow electrically induced velocities that characterize all the charged particles in the mist. Such equilibrium determines the maximum electrical energy available (potential) and locates the regions of maximum stress (field intensity). Above a certain not well-defined threshold value of field intensity, electrons in the regions of maximum stress obtain very high velocities in the small distances that separate gas molecules. Eventually they obtain such a high velocity (greater than 10^7 cm/sec) that they are able literally to break the molecule they collide with. The process is called ionization because it splits the target molecule into a positive ion and another electron. This new electron and the original one constitute two new potential "bullets". If the electric field is still adequate in the region where these two electrons find themselves, each one acquires again high velocity and reproduces the whole sequence. It is evident that, within the time it takes the original electron to make a few ionizing collisions, a very large number of ionizing events takes place. These liberate very rapidly increasing numbers of positive ions and electrons, and the process is appropriately called an electron avalanche. Because of their very small size, electrons move about 1000 times faster than positive ions. Consequently, they move away leaving concentrated funnel shaped "packages" of positively charged ions. In general, the avalanche either stops or leads to a new stage in the electrical breakdown sequence. However, under any circumstances and in contrast to the charged droplets of the mist, all the charge carriers liberated in an avalanche (including the funnel shaped package) may move, due to electrical forces, at velocities that are very much larger than any gas or water jet velocity in the tank. Clearly, these small charged particles try to destroy the equilibrium balance between electrical and mechanical forces in the mist. Whether they succeed in destroying this balance and, primarily, direction into the high field region. Such electrons cannot slow down or attach to electronegative molecules and are, therefore, rapidly removed by the metal surface leaving a stationary positive cloud of ions (not a dipole) in the region near the point. This produces an effective increase in the radius of curvature (available area) that also lowers the field and prevents ionization to take place. However, the resulting positive pulses are very different from Trichel pulses; they last 1 to 5 x 10^{-4} sec and liberate 10^7 to 10^8 ions depending on the radius of curvature of the metal point. Also, these pulses are not equally spaced; they occur at random primarily because some of the avalanches may, by chance, lead into a new ionization process called a positive streamer. The name is due to the fact that the ionization is no longer confined to the region of field concentration determined by the geometrical configuration, but it actually streams away from the region, even into one with no field. A positive streamer can roughly be described as a ball of highly concentrated space charge that, once formed near the point, is able to move and ionize independently of external electric forces.

When avalanches take place, the number of ions produced is just as large as the number of photons resulting from excitation and relaxation of neutral molecules and responsible for the characteristic bluish color of coronas. These photons are, of course, unaffected by electrical forces. In air they come from excited N_2 molecules, and some have enough energy to photoionize oxygen molecules. These randomly located photoelectrons are thus produced in the low field region at the same time that the avalanche is forming. When the package of positive ions left by the avalanche reaches a critical size, the field produced by its positive charge alone is high enough to cause appropriately located photoelectrons to produce new avalanches. There is then propagation of ionization away from the point, and this process, which repeats itself and can be considered to be continuous for all practical purposes, is a positive streamer. The propagation velocity of streamers is very high, being of the order of 5×10^7 cm/sec at the onset of positive coronas. These streamers eventually die many diameters away from the point; however, each one is able to liberate from 3 to 12×10^9 ions within a small fraction of a microsecond depending on the radius of curvature of the stressed point. This number of ions is for streamers that are much smaller than a centimeter in length. Larger points produce longer streamers that deposit around 1.5×10^{10} ions per centimeter traveled. Actually, the formation of long pulses (burst pulses) at the onset of positive coronas is quite critical and difficult to maintain. For all practical purposes one may consider the onset of the discharge only in terms of positive streamers.

In a region near the corona discharge, the number of net charges produced by splashing (between 10^5 and 10^6 ions/cm^3) is significantly smaller than the number of ions liberated by even a single ionizing event that takes place only within a fraction of a microsecond (either a Trichel pulse or a positive onset streamer produces at least 10^9 ions). It is clear, then, that the charged mist near the corona discharge is strongly affected by these ions. A "screening layer" of charge residing on mist particles is produced. This is similar in nature to one predicted to be present in natural clouds (Brown, et al., 1971; Vonnegut, 1953; Grenet, 1947), and its existence has been verified both in shore facilities (SUNY and Mobil) and in tankers (S.S. DAYLIGHT and S.S. PEGASUS). Ions from the corona discharge are propelled, as soon as formed, towards the region where the oppositely charged bulk of the mist that induced the discharge is located. As the ions start to travel in that direction, they are strongly attracted to the very much larger particles of the mist. The attractive force between ion and droplet is produced primarily by polarization fields that act on the ion and are due to a very strong dipole induced on the drop of water by the local electric field. For the droplet sizes and charges characteristic of the stable mist, this attractive force is practically independent of net charge on the drop. Consequently, the ions are collected by a relatively very few droplets near the corona discharge. These drops rapidly become charged with polarity opposite to what they had before the discharge started. A pocket of space charge residing on the droplets of the mist is thus produced; this space charge also stops the corona discharge. It is exactly a macroscopic version of the ionic space charge responsible for the submicrosecond pulses characteristic of all corona discharges. However, since the mist droplets are controlled not by electrical, but by aerodynamic forces, the time required for the renewal of the discharge depends now on the dispersal of space charge by gas motion. It falls in the range of many seconds, that is, at least a million times slower than the times involved in the dispersal of molecular ions. As noted, this is the reason why corona discharges act as a sink to maintain equilibrium, only through a slow droplet-droplet and not an ion-droplet interaction. The two processes operate on very different time scales.

The interaction between a corona discharge and its inherently produced space charge is then different when considering a metal two-electrode system (with its required external power supply) and a single electrode in a charged mist. In both tankers and shore facilities the discharges observed at protruding objects are exactly what is expected. Streamers or Trichel pulses last for a few seconds, then stop due to local charging of the mist. The corona can be reestablished either blowing away the space charge or rapidly moving the protruding object to a new region. Discharges are observed at rounded objects introduced deep into the mist or at the sharp corners of an object located only a short distance below the deck. At times discharge pulses have been observed that exhibit on an oscilloscope a characteristic shape that indicates corona discharges from drops of water either attached to or falling from larger objects.

At least at the onset stage, corona discharges are present during washing operations. Most probably they always take place only at the surface of a structural member that protrudes into the mist and incorporates an exposed local sharp point, such as a piece of scale, a square-cut corner, a thread on a bolt, or even an electrically distorted drop of water (English, 1948; Taylor, 1964, 1966, 1969; Barreto, 1969, 1971; Pisler and Atkinson, 1971). Note that this is also the optimum location for aerodynamic turbulent mixing. Locally, the corona produces a pocket of charge that resides on droplets of the mist, is opposite in polarity, and vastly exceeds the charge density value of the far-away equilibrium mist. The discharge stops and will not go on again until the pocket is well mixed with the rest of the mist. Clearly this is one of the switched-on equilibrium-control processes required. If, at onset, corona discharges are, or lead to, hazardous conditions, they must do so only under very special circumstances, since evidently tankers do not explode every time their tanks are washed even though it seems that very frequently there is a flammable hydrocarbon mixture in the tank.

Electrical Ignitions

It was noted that the possibility of an ignition produced by an electrical discharge directly or indirectly associated with the charged mist is the electrostatic problem concerning explosions in tankers. The discussion just presented makes it evident that electrical coronas between a sharp grounded metal object and the mist are not likely to proceed beyond the onset stage, and at this level of activity no ignitions are produced. This has been verified in the laboratory using point-plane electrode geometries, gaps smaller than 10 cm, and steady voltages. A metal (Klaver, 1971), charged plastic (Reynolds, 1963; Gibson and Lloyd, 1965) or hydrocarbon fuel liquid (Leonard and Carhart, 1967) has been used as the plane. It is necessary to consider now how ignitions are known to take place when triggered by electrical discharges. (See, for instance, Lewis and von Elbe, 1961, and Barnett and Hibbard, 1957).

It has been repeatedly stated that about 0.2 millijoules of electrical energy are required to ignite a hydrocarbon mixture. The conditions under which this energy is to be supplied to the discharge and, in fact, the reason why an absolute energy value is given as a limit have not been always noted. The typical ignition experiment from which this number comes considers an accurately measured small capacitor charged to a known voltage and connected with two electrodes located in a chamber filled with the flammable mixture to be tested. The electrode separation, pressure, temperature, and hydrocarbon content are all accurately monitored. The electrodes are always adjusted to produce only spark discharges. They are closely spaced parallel plates that provide a constant uniform electric field anywhere between the plates. The region of avalanche onset is then determined only by the location of free electrons, and there is no geometrical field concentration effect. In practice the edges of the plates cause deviations from truly uniform fields. Even if this is avoided by carefully shaping the edges of the electrodes (Rogowski profiles), the discharge is, of course, randomly located. This is the reason that in ignition experiments metal rods that are flush flanged by large glass plates are used. The metal rod at the center of the glass plate locates the region of breakdown, while the glass plates together with the rods provide a parallel uniform gap that results in a field not very much different from an all metal gap. (Since the voltage is raised very slowly, surface charge accumulates on the glass plates.) Free electrode tips or electrodes protruding through the glass are avoided because, if used, the conditions that specify the discharge must include exposed distances and curvatures.

The result of a typical experiment is given as the minimum amount of energy stored in the capacitor and required to produce an ignition plotted versus the distance between electrodes. At atmospheric pressure and for a small range of electrode separates (0.085 to 0.150 inches for a stoichiometric air-methane mixture), the energy curve exhibits a flat bottom at the often-quoted value of a fraction of a millijoule. No ignitions take place at smaller gaps (cooling by the electrodes), and longer gaps require, of course, larger energies. It is noted, however, that energies larger than the minimum are less efficient for producing ignitions at a fixed electrode gap. Clearly, this indicates that it is not only the amount of stored energy that is important, but also the manner in which it goes into the gap, i.e., the breakdown process. The reason a minimum absolute value of energy is required to cause an ignition is due to the fact that, like condensation, ignition is basically a nucleation phenomenon. For any given set of conditions it requires the formation of a flame of fixed critical size before a combustion wave can propagate. (The process is similar to that of a scientist doing electrostatic experiments inside of a square hole at the top of a mountain. In order to jump off the cliff of the mountain, he must come out of the hole, and to do so requires that he climb a very small distance compared to the one he is going to fall. He needs no energy to go down to the bottom of the mountain, but must obtain enough energy to climb a small critical height. Also, even if he has a great excess of energy, he must be able in a single attempt to climb the whole wall. If he is not able to do so, he will use all of his energy in his attempts, will become exhausted, but will remain inside the hole.)

The ignition experiments incorporate an electrode geometry that guarantees the discharge to be a spark. However, there is no real agreement as to when a discharge is to be called a spark, and, moreover, the reason is not a matter of definition, but rather of ignorance. It is known that avalanches progress into streamers; then, within a time period that may depend on geometries but always allows for the whole initial streamer process to be completed, a new, very strong ionization mechanism referred to as space waves of ionization begins (Loeb, 1966, 1968; Suzuki, 1971). These propagate almost at the speed of light and produce a conducting narrow hot channel. In a one-centimeter gap with a uniform field, the whole sequence from the start of the avalanche takes less than 10^{-7} sec. If a large supply of electrical energy is available to the discharge, it progresses to a stable new form--an arc. This is controlled primarily by heat and evaporation of the electrode material used and not by ionization of the air. An arc involves two electrodes, high temperatures, high currents, and low potential differences. It may play a role when considering the possibility of radio induced ignitions but has no role when considering discharges associated with the charged mist. If the amount of energy is limited but, nevertheless, available at a very high rate (viz., a charged capacitor), a hot channel forms and dies very rapidly. Its temperature, associated shock wave strength, diameter, visual appearance, and probably even the processes leading to its formation are all related, through incredibly rapid events, to the amount and rate at which the energy is available. No one can say if incipient arc conditions or merely gas ionization events are required for the formation of a hot channel. Arbitrarily, a spark will be considered here to be one only when the ionized channel behaves as a good conductor, and there is thermal equilibrium between electrons, ions, and neutral molecules. Some recent work (Suzuki, 1971) indicates that this only happens when the ion density in the channel reaches a value around 10^{18} ions/cm^3.

It is clear, then, that a discharge between two electrodes with large curvatures can easily produce an incendiary spark. As indicated by the ingnition experiments, the actual energy involved is very small; in fact, the required discharge can barely be heard or seen in a lighted room. (It is less intense than the typical discharge obtained trying to open a door in a nylon carpeted hotel.) Clearly, the amount of energy available in a charged mist or dissipated in the observed coronas is much larger than the amount required to produce an ignition. Nevertheless, it appears that the incendiary discharge must be a spark or a hot channel. The result, which is not surprising and is being carefully confirmed, indicates that the production of free radicals required to activate the chemical reaction is due to local heating and not to direct electron impact with the hydrocarbon molecules at room temperature.

The question immediately raised is whether a corona discharge between the mist and grounded electrode can ever progress to produce a hot channel. After all, lightning discharges do come from clouds, and, by rapidly compressing highly charged aerosols, it is possible to produce actual sparks from an aerosol to a grounded object (Barreto, 1969). There is no good, specific argument to exclude lightning-like discharges because no one really knows how they get started. The maximum charge densities involved are comparable to those in tankers, but the volumes are very much larger. Lightning does start with corona discharges inside the cloud; however, in an isolated net charged cloud these are not neutralizing, but charge redistributing events that are believed to lead to the establishment in clear air of high fields (20-30 kv/cm) over large distances (decimeters) (Loeb, 1970). Apparently, these fields are required to launch the first visible evidence of the discharge on its way to the earth (the stepped leader phase). They are possible in a real cloud because there are no grounded rough walls with protrusions confining the mist. Such fields cannot occur in a tanker because induced coronas will lower the charge density long before they can be attained. The compressed aerosol experiment is, at the moment, merely an uninvestigated laboratory curiosity that falls in a different ball park, but illustrates what it takes to get a spark out of a small aerosol volume.

It is possible only when supersonic velocities are used for the compression and with charge densities in the mist of the order of 10^{10} to 10^{11} ions/cm^3.

High voltages may be applied to a metal point-plane gap very rapidly. If a voltage pulse with a rise time of approximately 10^{-7} sec or smaller is used, it is possible to accumulate charge on the stressed electrode much faster than it can be affected by the ionization process in the gap. This is called an overvolted gap because, for a very short time, the electric field may be made much higher than the ionization onset value using a steady voltage. The resulting streamers are stronger than those in a regular corona and exhibit a longer range that depends, of course, on the magnitude, rise time, and duration of the applied voltage pulse. An incendiary spark can be produced in an overvolted point-plane (one centimeter) corona gap even though the energy is limited to values near the ignition threshold. The reason is, of course, that the pulsed streamer leads directly to a spark and actually prevents a corona discharge (many smaller streamers) from taking place. When connected to a steady voltage supply, the same gap produces only a harmless corona that may, nevertheless, dissipate an unlimited amount of electrical energy.

Using large rod-plane gaps (7/8" diameter spherically capped rod 20 to 30 cm from the plane) and very high pulsed voltages (100-200 kv with a rise time around 10^{-7} sec), it is possible to produce a discharge that is <u>not</u> a spark but ignites a propane-air mixture. Again, the same gap with a steady voltage produces long streamers, but no ignitions. At the moment it is not clear how this pulsed discharge ignites without producing sparkover. It is believed that the initial pulsed streamer dies and does not appreciably reduce the field. The ignition could then be produced by selectively located avalanches that are triggered by the electrons left by the pulsed streamer. It is clear, however, that overvolted gaps provide the only situation under which coronas have been made to ignite hydrocarbon-air mixtures at atmospheric pressure and temperature. In practice, an overvolted gap may be produced using only an actual spark, or, arc discharge. Therefore, ignitions produced by such overvolted gaps do not apply at all to the tanker problem.

Corona discharges of the type required to produce an ignition do not occur between the charged mist and any solid object in the tank. In fact, corona discharges at the wall are sinks of charge that limit the charge density value and prevent the formation of lightning-like discharges. On the other hand, if a two-electrode system is somehow provided, an ignition is easily produced by a low energy spark across the gap. The formation of this spark requires a more or less geometrically uniform field at a threshold value given by the often quoted 3×10^4 volts/cm. The minimum threshold energy involved is the 0.2 millijoules value and must be available at a very high rate from a charged capacitor. This capacitor in turn provides a relationship between the physical sizes of the gap and the charged object involved in the spark discharge. For instance, if the energy is stored in a charged sphere of radius, a, facing a metal plane with a gap distance, ℓ (air at atmospheric conditions), it is easily shown that in order to produce an ignition

$$a\ell^2 = 0.218 \text{ cm}^3.$$

The minimum possible gap is the quenching distance for ignition (0.22 cm for a methane-air mixture); this corresponds to a sphere 4.5 cm in radius (about the size of a softball) charged to 6600 volts (Klaver, 1972). Alternatively, a sphere only 0.87 cm in radius (smaller than a golf ball) charged to 15,000 volts may produce an ignition across a 0.5 cm gap.

A falling charged object is, of course, the primary ignition suspect. However, it is not clear how such an object is able to obtain sufficient charge from the mist in a tanker. In fact, this is, perhaps, the critical result needed to explain the explosions. Experimentally, spheres with a sharp point attached to them are able to go into corona when passing near a charged aerosol. In this manner they are able to obtain sufficient charge to produce ignitions when falling into a metal plane. Also, bodies (van de Weerd, 1971) collected after falling through a charged mist in a large tank have exhibited inconsistent charge values near the critical dangerous level. Nevertheless, it must be emphasized that besides a falling body one can easily imagine many other ways to provide a two-electrode system that would lead to an ignition. For instance:

a) surface charge on a thin dielectric coating of a metal may puncture and produce a hot spot (common in electrostatic precipitation),

b) a charged dielectric film rapidly being peeled from a metal or dielectric surface may produce an air spark (Texaco experiment),

c) a metal object resting on a thin dielectric (wax, oil) may go into corona and obtain enough charge to produce a spark through its support,

d) an isolated long object introduced into the tank (water, metal, or even a dielectric substance isolated for a sufficiently long time) may obtain enough induced charge to sparkover through air to a nearby surface (Shell experiment).

Note that the required condition is, however, always the same: a capacitor with, effectively, two electrodes.

Conclusions and Recommendations

This report combines specific, recently obtained results, motivated by a rush to solve a serious economic problem, together with well-established facts and basic laws that must be satisfied and applied to evaluate the hazard due to static charges in tankers. It has been demonstrated that, indeed, a hazard does exist that is associated with the production of a net charged mist during tank cleaning operations. However, the formation, evolution, equilibrium and interaction of the mist with the walls or with objects introduced into the tank is a complicated, interdisciplinary affair that goes far beyond electrostatics. Great care must be exercised in extrapolating laboratory results to actual tanker operations. A complete evaluation of the manner and processes that may lead from generation of the mist to ignition by a spark involves, in addition to electrostatics, problems in chemistry, electro and fluid mechanics, particle and surface physics, and even combustion engineering. Some of the information required is not available either because it has not been compiled, or because the phenomenon in question is not understood. Consequently, at this stage, neither enough understanding nor pragmatic information has been accumulated to predict when an ignition may occur. However, the requirements that must be satisfied to produce an incendiary discharge have been established. It is believed that, for the first time, the problem has been clarified to a level at which we may recognize important parameters, some of their interrelationships, the gray areas of understanding, and, particularly, the manner in which all of these factors must be evaluated in order to decide on accident prevention measures.

The report has not been prepared for the expert in each area considered but, hopefully, for all people concerned with the tanker problem. Therefore, it is useful to list the main results together with the heading of the section in the text where they are considered.

I. Production of the Charged Mist

a) Charging is due to breaking the surface of water at the regions of splashing, predominantly at the wall of the tank. The amount and net polarity of the charge produced, under a given set of conditions, is not generally known. However, it could be predicted by careful calibration of chemical and kinetic interactions at the surface of water. Hence, controlled laboratory experiments, measuring the effect of the many parameters involved in charge generation by splashing, could provide tabulated data to determine the charge generation ability of a given combination used during actual washing. For instance, such data exists and is used to predict the charge obtained by spraying different concentrations of salt in water at different pressures.

b) Aerodynamic turbulent mixing has been shown to be not only very effective, but also the controlling factor of the electrical properties of the mist. This is because of a characteristic, very small electrical mobility of the charged particles. The result is of paramount importance because it guarantees that monitoring the electrical parameters at selected fixed positions provides information of the whole mist in the tank. However, care must be observed to insure that the monitoring equipment does not go into corona and that the equipment itself is not a hazard. It is clear that isolated large pockets of space charge do not exist; nevertheless, the mist is expected to have a large population of droplets of both polarities superimposed on the net charge density measured.

c) The charge generation ability of water is altered by chemicals, and their effect has been noted in tankers. There exists, therefore, the possibility of controlling or preventing charge generation by the use of chemical additives. Controlled laboratory studies, much the same as those indicated under (a) above, should be undertaken to explore this possibility.

II. Mechanical Properties of the Charged Mist

a) The typical particle at equilibrium in the mist during washing must be able to survive coagulation and settling effects in a turbulent atmosphere. This limits their size to a range given approximately by $10^{-5} < r < 5 \times 10^{-3}$ cm. A much wider spectrum, of a transient nature, is produced at the region of splashing; accordingly, the range just noted represents possible sizes in a well-mixed turbulent region away from the walls of the tank.

b) Charged droplets produced by induced corona discharges constitute an effective sink of charge that, at equilibrium, is required to counterbalance the generation of charge by splashing. The balance is maintained not by fast ion-droplet interaction, but, rather, by droplet-droplet interaction. This is a much slower process compatible with the time required to attain equilibrium through turbulent mixing. (See also III(b) below.)

III. Electrical Properties of the Mist

a) Considering uniform charge density and an effective volume given by that of an inscribed imaginary sphere inside the tank, a simplified theory provides surprisingly good agreement with experimental data obtained both in shore tests and in tankers. This result confirms the effectiveness of turbulent mixing and the measurement of practically constant space charge density.

b) Induced positive or negative corona discharges occur during the washing of the tanks. The computed number of charges liberated by these discharges under the worst possible conditions insures that they are capable of constituting an effective sink of charge during washing. The attachment to the droplets in the mist of the ions produced by the corona discharges not only limits the turbulent space charge density, but guarantees that the coronas will not progress much beyond the onset stage.

c) The change in the size of a tank is of such practical importance that expanding the meaning of (a) and (b) as related to tank size is justifiable. In a tank that has been washed long enough to obtain equilibrium, there is a balance between sources and sinks of charge. The efficiency of the sources is evaluated by the charge density, and that of the sinks, by a specified electric field (or potential) required for the maintenance of the corona discharges. At equilibrium this field, the charge density, and the size of the tank are all related through a constant (E = const. ρx). It follows that changing one parameter implies changes in the other two, and the effect cannot be properly evaluated by reading a single variable ($dE \approx \rho dx + x d\rho$). For instance, if the electric field required for the onset of coronas is the same at the wall of two different tanks ($dE = 0$), the larger tank will exhibit a lower charge density ($dx \approx -d\rho$). On the other hand, if in the same tank ($dx = 0$) the source is made more intense (high volume fixed machines), both the electric field (corona activity) and charge density will increase as specified by a new equilibrium condition ($dE \approx d\rho$). (These changes were observed in the S.S. PEGASUS.)

IV. Electrical Ignitions

a) In order to produce an ignition in a tanker, a hot spark discharge is required. This is because the number of free radicals produced by electron collisions in a cool discharge (electrons obtaining energy from the electric field) can never reach the critical density required for the onset of the chemical reaction. On the other hand, thermal dissociation may easily produce the population of free radicals required to nucleate a combustion wave.

b) It has been verified that, indeed, the amount of electrical energy required to produce an incendiary discharge is very small. However, since a spark is required, this energy must be supplied to the gas discharge in a very particular way, which always implies basically two electrodes, a more or less uniform field in the gap between them (no coronas), and a capacitor able to supply its stored energy at a very high rate. Isolated, properly shaped, charged plastic or liquid surfaces may constitute one of the required electrodes.

c) Falling objects the size of an orange charged to approximately 6.6 kilovolts are able to produce incendiary discharges. Alternatively, smaller bodies at higher voltages can also do the same. Besides a falling body, there are many other possible two-electrode capacitor systems that may produce an ignition in a tanker. Some of these were listed, but there is no way to assess their probability for ignition compared to that of a falling body. The very specific conditions required to produce a spark in a tank are probably related to a very small chance for an explosion during washing operations.

d) The production of a corona discharge capable of producing an ignition invariably requires the use of a spark. The corona discharges produced during washing of the tanks are unable to produce an ignition. Moreover, their presence excludes the possibility of lightning-like discharges.

The possibility of a low probability event triggering an incendiary electrical discharge, under the conditions produced during tank washing, has been demonstrated. Although the process leading to this discharge has not been specified, the type of discharge and the requirements for its production have been established. At this moment, there are at least four possible approaches to solve the explosion problem:

chemical additives, mixing of an oppositely charged mist, dividing the tank volume into electrically smaller volumes (grids, wires), and inerting. Which one or how many of these approaches is to be pursued is a management decision for which scientific information constitutes only one input.

Acknowledgments

The results just presented are my understanding of the oil tanker problem. It does not necessarily represent that of other people within the oil industry with whom every aspect has been repeatedly discussed during the past two years. There has not been time to prepare journal articles; therefore, a list of the memoranda and reports used is included in the references section. However, I am sure most of the work has been done through heated arguments, of which there is no record. There is no way to know "whose idea it was" because this was never the point of the arguments with W. Bustin (Esso), R. Klaver (Chevron), R. Lange (Mobil), and the people at Shell in Amsterdam. I want to ask their forgiveness whenever their ideas come through the report without proper acknowledgment. If they disagree with the results, well, that is the purpose of the meeting for which this report is prepared.

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