

Zeitschrift: Bulletin der Vereinigung Schweiz. Petroleum-Geologen und -Ingenieure
Herausgeber: Vereinigung Schweizerischer Petroleum-Geologen und -Ingenieure
Band: 26 (1959-1960)
Heft: 71

Artikel: Problems in connection with static electricity in the petroleum industry
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DOI: <https://doi.org/10.5169/seals-190185>

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Problems in connection with static electricity in the Petroleum Industry

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In the handling of materials certain electrical phenomena, usually referred to as «static electricity», frequently occur. Movement of the material which is inherent in such handling leads to what is commonly called generation of electricity, viz. a separation of positive and negative charges. This is a small enough effect in itself, but one which becomes noticeable if there is some means of accumulating the separated charges.

Charges may be generated as a result of the flow of fluids or of particle-laden gases, such as jets of steam or carbon dioxide, all of which have occasionally led to accidents.

The charges entrained by the flowing material may accumulate within such material itself if it has a very low conductivity (white hydrocarbon products, clouds in gases), on solid insulators or on conductors of electricity if these are well insulated (e.g. on vehicles with rubber tyres).

Consequently, in view of the generality of both generation and accumulation, there are a great number of situations in the petroleum industry where harmful electrification has been observed. An investigation into the causes of an accident will invariably have to consider several alternatives. All this adds to the complexity of preventing accidents caused by static electricity.

Accumulation on an insulated conductor is the mechanism which most easily creates a spark of sufficient intensity to be incendiary. It is, however, also the mechanism which is most easily safeguarded against, viz. by bonding. As a result accidents of this nature have become comparatively rare; however, overlooking an insulated conductor remains just as dangerous as not knowing the rules.

An important group of accidents is that in which charges have collected within a strongly insulating hydrocarbon liquid, ultimately leading to sparks in the adjacent air-

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vapour mixture. This group includes explosions in storage tanks in the process of being filled or whose contents are being stirred.

These accidents can be prevented by making the liquid slightly conductive. In all such accidents the product involved will be found to be a white one (heavy gasolines, JP 4's, light kerosines), never a material such as a crude oil, because the latter type of product is too conductive to allow a charge to accumulate within it.

A water-free product may become charged by being passed rapidly through a pipeline or and even more strongly so by passage through a filter, but in storage tanks or refineries and depots the flow rate of the incoming liquid is usually not extreme. In this case the presence of a second liquid — usually water — is very important, because very strong fields are observed in the tank if such a liquid is emulsified in the hydrocarbon, e.g. by pumping the two together to such a tank. Strong fields — up to several 100 kilovolts per metre — are also produced if the water bottoms are stirred up in the tank. It is clear that in this case the settling of charged drops of water provides the transport of electricity.

In this group of accidents, contrary to the belief sometimes expressed, the humidity of the atmosphere outside the tank has no influence whatsoever. The specific electric conductivity is conveniently measured in units of $10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1} = 10^{-12} \text{ ohm}^{-1} \text{ m}^{-1}$, which may be referred to as picomho/m or, more simply, as conductivity units. Representative figures are:

most white products	1—10 conductivity units
crude oils	10,000—100,000 conductivity units

Practical experience with white and dark oils indicates that products will be safe at conductivities above some value intermediate between these two ranges. It was an object of research to define this value. Such a value must depend on the intensity of the charging mechanism envisaged for the particular type of product. A safe conductivity may always be reached by a mixture of crude or asphalt, but this would spoil the product's properties. It was therefore a further object of the oil companies' researchers to develop a potent additive capable of being used in such small concentrations that it has no side-effects.

As mentioned earlier, there are a number of situations where charges generated in a flowing liquid collect on insulated metal bodies which may then spark against other conductors. Examples are:

- a) filling of rubber-tyred tank cars through non-conducting hoses;
- b) gauging and sampling of tanks in the process of being filled;
- c) use of insulated stirrers in tanks.

Although in some of these cases, particularly b and c, an additive may be of some help, the primary measure to take is earthing or bonding.

In the cases of charging by steam and carbon dioxide jets the primary precaution is also electrical bonding. In extreme cases this may not be sufficient; in particular for CO₂ there is conclusive proof that incendiary sparks may be produced between the cloud and totally bonded surroundings.

Considerable research effort has been devoted to this field in recent years, in particular by some of the oil companies. Mention may be made of two Shell and two Esso papers presented at the November 1957 meeting of the American Petroleum Institute, a full account of Shell's research and development work¹⁾ and an Esso paper at the Vth World Petroleum Congress held in June 1959.

There is general agreement on the conclusion that the additive approach is considered most attractive, and also on the desired level of conductivity.

As already mentioned, an additive does not cope with all of the foreseeable situations, and we shall therefore proceed to discuss safeguarding operations more generally.

Safeguarding Operations

The safety measures dealing with static electricity can be conveniently grouped in the following order.

- A. Prevention of explosive gas mixtures.
- B. Removing electric charges by means of earthing and bonding.
- C. Removing electric charges by means of antistatic additive.
- D. Reduction of generation of static electricity.

This is a natural order in which each following item should be considered if the earlier ones cannot be or have not been applied, or, in the case of B, could not be a complete success.

A. Prevention of Explosive Gas Mixtures

From the literature ¹⁾ it can be established how the volatility of the products affects the upper and lower ignition temperature, the volatility being given by either the Reid vapour pressure or the ASTM initial boiling point. It follows that at ambient temperature in a temperate climate the products known as heavy gasolines or naphthas are most likely to form explosive vapours under equilibrium conditions. However, not too much reliance should be placed on the fact that a product nominally lies outside the danger zone. At least six major fires with kerosines are known to have occurred below the flash point. Here the vapours presumably have been enriched by contamination with gasoline or by fog formation. The major disaster in 1951 at Avonmouth (UK) was traced to a tank being splash-filled with a gas oil which was found to be contaminated with gasoline.

All kerosines should be considered liable to form explosive vapours. A similar argument holds true, though to a lesser extent, towards the gasoline end of the range of white products, where dangerous vapours are present in the initial stages of filling of empty tanks and will remain at higher levels in the tank for a considerable time. Moreover, certain gasoline components are definitely in the dangerous zone of volatility.

Some of the safety measures to prevent explosive gas mixtures have themselves proved to be dangerous, if applied in an improper manner. Both steaming and carbon dioxide blanketing have led to grave accidents (tanker explosion, see 1), p. 19; NATO tank at Bitburg). Floating roof tanks, too, have suffered from fires due to improper bonding of the roof. Here the floating roof collects charge by induction in the atmospheric electric field during thunderstorms. If the electrical conditions suddenly change, for instance after a stroke of lightning, the induced charge is freed on the floating roof and has to flow away to earth. If the roof is insufficiently bonded there may be a spark discharge between the rim of the roof and the tank shell, leading to a fire in the rim space.

B. Removing Electric Charges by Means of Earthing and Bonding

Ideally the product to be handled should be in contact only with conducting bodies, and these should all be electrically bonded. Thus, if a liquid is charged positively in a pipeline and then fed into a tank, the bond provides the path for reuniting the positive charges collecting on the tank wall with the negative ones remaining on the pipe wall. Earthing is not essential. The earthing of all bodies liable to become charged is merely

a convenient means of providing a bond between them, but there is no net flow of electricity to earth.

For the purpose of protection against electrostatic charging the application of special earthing or bonding connections is usually superfluous. The currents generated are only of the order of microamperes, and accordingly the voltage differences caused over the resistances normally encountered between, for example, various pieces of refinery equipment are completely negligible. Bonding is, however, necessary, for instance when filling a rubber tyred vehicle through a rubber hose (tank truck, aircraft).

However, it should be emphasized that earthing and bonding of all conductors are in themselves not sufficient to do away with electrostatic hazard, for when charged and highly insulating fluids are pumped into metal containers, appreciable fields are set up within such containers, field strengths of several hundred thousand volts per metre having been found, and these may be further increased near edges and points.

C. Removing Electric Charges by Means of Antistatic Additive

The electric field in the hydrocarbon liquid being handled, and consequently the field in the adjoining vapour space, can be drastically reduced by the addition of a dope meant to raise the conductivity. Such a dope is not necessarily antistatic in the sense that it suppresses the generation of electricity; its function is rather to raise the conductivity of the liquid to a higher level. This level depends on the type of handling which the product is expected to undergo. Though 20—50 conductivity units is an adequate level for the usual handling in refineries, high speed aircraft fuelling, where filters are involved, requires about 200—500 conductivity units to reduce electric fields within tanks to negligible proportions.

It should be stressed that the application of antistatic additive is meant to be complementary to the rules on bonding and earthing mentioned previously. For instance, impossibly high conductivities would be required if in the filling of tank cars or the fuelling of aircraft such bonding were to be achieved through the column of liquid contained in the filling hose.

D. Reduction of Generation of Static Electricity

This section deals with good housekeeping in refineries and depots. One very important point is not to mix water and oil in the pipelines.

If such mixtures cannot be avoided, e.g. when the oil in a line is being replaced by water or vice versa, the flow rate should be limited. So far the precaution of keeping the linear flow velocity down to 1 m/sec has proved quite satisfactory. The purpose of this practice is to prevent the creation of very intimate mixtures of water and oil, so that the water will settle out easily and rapidly in the storage tank. The flow velocity should not be much below 1 m/sec at this stage. At lower velocities pockets of water will remain in the line and the reappearance of suchwater after the velocity has been increased constitutes a hazard again.

The Use of Antistatic Additives

In the report ¹⁾ a practical antistatic additive is mentioned about which further information is contained in ²⁾. This additive is supplied in the form of a solution to be applied in a dosage of 2 kg/1000 m³. It contains two active ingredients, since it is based on the fundamental discovery that two suitably chosen substances will together impart

to a petroleum product a conductivity far higher than the sum of the conductivities each substance would have caused separately. This finding has made it possible to formulate additives whose activity is unprecedented, i.e. it has become possible to reach the desired conductivity while complying with the specification tests for the various products. The two ingredients are the chromium salt of an alkylated salicylic acid and the calcium salt of a dialkyl ester of sulphosuccinic acid. The solvent is a hydrocarbon.

At the prescribed dosage the conductivity obtained depends on a number of factors, such as the temperature, viscosity and aromaticity of the product. Furthermore, there is an aging effect, particularly in the presence of water. A freshly doped solution will change its conductivity during storage. Usually this aging effect, which is generally observed with electrolyte solutions in hydrocarbons, leads to a decrease in conductivity. The relatively slow rearrangement of the molecules and ions that will take place after the additive concentrate has been introduced into the hydrocarbon liquid may well play an important part in this phenomenon. A hydrocarbon liquid freshly doped has a conductivity which may be twice as high as the value found for the same doped product measured after a fortnight. The major part of this drop in conductivity appears to occur during the first three days following the doping and, after about two weeks, the conductivity remains approximately constant.

The aging is not considered to be of practical importance, since the freshly doped oil products at the recommended doping level have much higher conductivities than is required.

Scope of the Additive

From the discussion under A it follows that the following products should preferably be doped: motor gasoline, heavy gasolines, such as heavy platformate, JP4, kerosines (illuminating kerosine, aviation kerosine, dual purpose kerosine, tractor vaporizing oil), and some special products.

Such products would then be safeguarded all the way from refinery tanks through tankers and depots to the consumer's storage.

For most of the products mentioned above an oil company can decide for itself as to whether or not to use the additive. Such clearances have in fact been given within the Royal Dutch/Shell Group.

For aviation fuels (kerosine and long range fuel JP4), however, permission by the appropriate authorities is required. Such permission can only be expected if an anti-static additive is of definite advantage in the fuelling of aircraft. It is already known that electric fields in aircraft tanks are by no means negligible, but further developments will have to await a definite assessment of the risk of producing incendiary sparks during fuelling.

Literature

- 1) «Electrostatics in the Petroleum Industry», Elsevier Publ. Co. (Amsterdam 1958) by A. Klinkenberg and J. L. van der Minne.
- 2) «Technical Bulletin on Shell Antistatic Additives, ASA-1».

