LITERATURE SURVEY

on

LONG-TERM STORAGE OF
PETROLEUM PRODUCTS

ARMAMENT RESEARCH PROBLEM

Contract W33-015-Ord-5733
Submitted May 31, 1946

0-997

Battelle
Memorial Institute
505 King Avenue
Columbus 1, Ohio
May 31, 1946

Office, Chief of Ordnance
Engineering Branch
Artillery Division
Industrial Service
Washington, D.C.

Gentlemen:

Reference: CO No. 400.112/5517 SPOIR

In accordance with the instructions of your letter of April 9, 1946, regarding the reports on long-term storage, we are mailing to you the eighteen (16) copies of the report on "Petroleum Products".

Distribution of the balance of the copies is being made directly, and Cleveland Ordnance is being notified of the completion of this report.

Very truly yours,

Edward E. Slowter

Enc. (18)

cc: District Chief
Cleveland Ordnance District Office
1006 Terminal Tower Building
Cleveland 13, Ohio
LITERATURE SURVEY

ON

LONG-TERM STORAGE OF PETROLEUM PRODUCTS

ARTILLERY STORAGE PROGRAM

Prepared by

BATTLE MEMORIAL INSTITUTE

Contract #33-019-Ord-5333

Submitted May 31, 1946
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Distribution Sheet
LITERATURE SURVEY
on
LONG-TERM STORAGE OF PETROLEUM PRODUCTS
ARTILLERY STORAGE PROGRAM
from
BATTELLE MEMORIAL INSTITUTE
Contract W33-019-Ord-5333
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SUMMARY

A literature survey has been conducted on the long-term storage of petroleum products, which might be suitable for use in the storage of Ordnance material in suitable vessels. The available information on this subject in the Ordnance Department files at Battelle Memorial Institute has been reviewed, and a careful search of the literature for the past forty years has been made.

The various methods for storing petroleum and petroleum products are discussed in this report. Realizing that deterioration of petroleum products does occur, and that such deterioration is caused by contact with various metallic and nonmetallic substances and the atmosphere, and influenced considerably by temperature, light, moisture, and many other factors, an attempt has been made to show the influence of such materials and factors. The various methods employed to lessen these effects have also been considered.

The oils found most suitable for storage media should probably be closely related to transformer or turbine oils. In addition to being
carefully prepared, they should contain inhibitors to lessen the natural deterioration of the oil, and storage conditions should be such as to minimize contact with the air. The use of an inert gas layer above the oil will be of benefit in maintaining the oil in good condition.

INTRODUCTION

The long-term storage of ordnance material in an oil medium has been proposed as a means of preserving such material so that it will be usable at some future time. It is the purpose of this survey to consider such a method, and determine the effect of storage, not only on the military equipment stored, but also on the oil.

The literature survey was conducted principally by reference to original articles occurring in technical magazines, and to the following indices: Chemical Abstracts, British Chemical Abstracts, Industrial Arts Index, and the Engineering Index. All available books pertaining to petroleum technology were examined and any pertinent references were further investigated.

The Ordnance Department files available at Battelle Memorial Institute have been consulted, and some pertinent information was obtained. These references are included in the bibliography.

The findings of this survey follow.
Petroleum, as it exists in nature, is a complex mixture of hydrocarbons with which are associated small amounts of compounds containing sulfur, oxygen, and nitrogen. Certain inorganic constituents are sometimes present; these constituents may be salts in solution in the water emulsified with the oil, or they may be metallic salts of the acids associated with the petroleum. The petroleum, as it comes from the wells, is often emulsified with water, containing sometimes 50 percent or more of water. The removal of the water from these emulsions is often a problem, and many processes involving physical and chemical treatments have been developed.

The composition of petroleum varies according to the source, and there are differences in the petroleum obtained from different wells in the same field. The composition of the petroleum has a profound influence on the methods of refining and on the character of the final products. However, with the recent advances in petroleum technology, the objectionable characteristics of certain oils have been overcome and the final products have found their place in industry and commerce.

For purposes of classification of petroleum, a system based on the relative amounts of paraffin wax and asphalt has often been used. A petroleum which contains large amounts of paraffin wax and very little asphalt would be classed as a paraffin-base petroleum. The petroleum obtained from the Oil City and Bradford areas in Pennsylvania are excellent examples of paraffin-base oils. Those petroleum which contain a large amount of asphalt and little or no paraffin wax are classed as
asphalt-base. Petroleums from the Gulf Coast and California belong to this class. Intermediate between these classes are those oils which contain both paraffin wax and asphalt, and these petroleums are referred to as mixed-base oils. This system of classification is not perfect, and there are certain petroleums which differ widely from those usually classified in this manner.

Another system of classification (2) is based on the predominating classes of chemical compounds present in the petroleum. Those petroleums in which the majority of chemical compounds present are the homologous members of the methane series of hydrocarbons belong to the methane type of petroleum. A second type of petroleum, known as the naphthene type, is characterized by the presence of a large proportion of those compounds belonging to the naphthene class of hydrocarbons. Intermediate between these two classes of petroleum is the methane-naphthene type of petroleum. Polycyclic compounds are present to only a very small extent in the foregoing three types of petroleum. A fourth class of petroleum, which is most unusual and rare, is the aromatic type of petroleum. This type is characterized by the large proportion of aromatic compounds, of which benzene is the simplest member, in the oil. A fifth class includes members of the methane, naphthenic and aromatic series of hydrocarbons in the petroleum, and this type has a preponderance of polycyclic aromatic compounds and naphthenes. The sixth class is comprised principally of aromatic and naphthenic hydrocarbons in which the ring structure is quite complicated.

Other systems of classification have been devised and have been found to suit the purpose of the investigator in explaining ab-
normalities in refining and behavior of the finished products. However, and in most cases, a combination of these two systems of classification of petroleums will suffice.

As mentioned previously, the advances in petroleum technology have brought about considerable changes in the petroleum products offered today, as compared to those available only a few years ago. Straight-run distillation of petroleum and petroleum fractions has given way to various thermal- and catalytic-cracking processes. The chemical treatment has changed from the straight acid and alkali treatment until today we have, in addition to the treatments with sulfuric acid and oleum, those in which aluminum chloride, salts of lead, magnesium, copper, sodium, and other metals, adsorptive materials such as fuller's earth, activated alumina, and silica gel, and many other materials whose purpose it is to confer specific properties to the final product, used in the chemical refining of petroleum. By means of the physical and chemical methods of refining, the producer has been able to present to his customers products which are extremely stable and reasonable in price. The stability of the products is reflected in increased resistance to oxidation, polymerization, and tendency of the oil to corrode metallic parts. The use of additives has become widespread, and, in addition to the improvement in resistance to oxidation, polymerization, and tendency to corrode, additives have been developed which will increase the oiliness, improve the viscosity index, and lower the pour point of lubricants, improve the detonation characteristics and lessen the tendency to form deposits of motor fuels, and improve the general characteristics of greases.
Despite all of the improvements in petroleum products, very little information is available on their use over a long period of time, or even on the conditions of use. The best information on long-time usage of petroleum oils comes from those who have been using transformer and turbine oils, and there are reports on these oils and the changes which have occurred over a period of approximately thirty-five years of use. This will be discussed more fully in the following pages.

**STORAGE OF PETROLEUM AND PETROLEUM PRODUCTS**

From the early beginnings of the petroleum industry, the storage of the crude petroleum and petroleum products has been a great problem. Many factors must be considered in order that the economy of the industry be preserved, and the operating costs of the individual companies be maintained at a competitive level. Each producer and refiner is confronted with space limitations resulting sometimes in a crowded condition not wholly compatible with safety and fire protection. However, every effort is usually made by the producer and refiner to prevent losses by leakage and vaporization, and constant vigilance and development has enabled them to succeed in their efforts. Corrosion of the container, deterioration of the stored product, and the formation of deposits through such action are problems that must be met and solved at each installation. Generalized and specific information on storage and its problems is available and will be discussed in the following paragraphs.
Storage in Earthen Reservoirs

The simplest method of storing crude oil is in an earthen pit or trench. These pits or trenches are constructed by removing the earth from an area to a desired depth, and lining the bottom and sides of the excavation with a plastic clay and water mixture. Sokolovskii\(^3\) reports the use of soil colloidal material (clay) saturated with sodium salts in the construction of earthen storage pits for petroleum products. It is claimed that apolar liquids such as petroleum products may be stored without loss. Results obtained with this type of storage reservoir indicate that kerosene may be stored for eight months and gasoline for two months without loss. Obviously, these earthen pits were covered. Contrasted with these results, James\(^4\) reports that crude petroleum stored in open earthen pits has been known to shrink as much as 40% in 15-20 days, due to seepage and evaporation of the lower boiling constituents of the petroleum. Contamination of the oil in the earthen reservoir by rainfall or surface drainage is a factor which must be considered, because difficulties in handling and refining might ensue.

Storage in Wood Tanks

Wooden storage tanks are quite often used for the intermediate storage of petroleum. The crude oil obtained from the well is transferred to a wooden storage tank and from there is pumped or drained into the collecting pipe line which transports the oil to a central storage area, loading dock, or to a refinery. These tanks are seldom very large, and they are used in areas where it would be difficult to locate a pra-
fabricated steel tank. They have numerous disadvantages, such as tendency to leak, general disintegration due to action of the oil and poor fire resistance. Wooden tanks are seldom used for the storage of petroleum products.

Storage in Steel Tanks

Much has been written on the general subject of storage of petroleum and petroleum products. Most of the articles have been concerned with materials of construction, types of storage vessels or containers, arrangement of bulk storage stations, safety, engineering information on petroleum, petroleum products and equipment, and of the trends in storage plant design. Hutchins and Burrell\(^5\) state that local factors determine the location, size, and material of construction of the tanks. Hilles\(^6\) discusses various storage methods, particularly for volatile products, and stresses safety in handling of these materials. Burk\(^7\) discusses the various factors pertaining to storage and transportation of oil products. His article is interesting, because it covers the practice in Germany. Yackey\(^8\) and Larsen\(^9,10\) discuss the general and practical aspects of storage of petroleum, petroleum products and other volatile oils. Singer\(^11\) presents an amplified bibliography on the storage and transportation of oil products for the year 1927, but no follow-up articles of this type under his authorship have been found. Leduc\(^12\) has presented considerable engineering data on friction coefficients and viscosities, which are of value in the design of pipe lines for the transportation of petroleum and petroleum products.
Because of its relative cheapness and ease of fabrication, steel tanks have been used to a very large extent in the petroleum industry. These tanks may be of several types, vertical, horizontal, or spheroidal, and they may operate under atmospheric or elevated pressures. Many of the older tanks were of riveted construction, but in recent years welded steel tanks have met with favor. These tanks are usually constructed according to standards set up by the various oil companies, and many times are constructed according to the standards of some technical society such as the American Society of Mechanical Engineers or the American Petroleum Institute (13).

Nicholson (14) discusses the pertinent points to consider in selecting, installing, and caring for steel storage tanks. Emphasis is placed on specifications for the tanks and arrangement of piping. Dowie (15) claims that the best type of container for storing petroleum and petroleum products is the all-steel tank of gas-tight construction. Bean (16) gives information of considerable interest on construction of tanks for installation above the ground. This article is intended for the design of tanks used in bulk storage stations, but the principles given here apply to any type of storage installation.

During World War II, and because of the shortage of steel plate, many tanks were moved from one location to another, and many other tanks were constructed from reclaimed steel. It is claimed that tanks constructed from reclaimed steel cost approximately 80% of the price of an identical tank built of new material. Information is given on inspection for salvage value, dismantling, reconditioning plates, construction, and welding (17).
In order to cut down evaporation losses, particularly in low-boiling mixtures such as gasoline, storage of the oil under pressure is often resorted to. While the reduction of losses due to evaporation will be discussed in later paragraphs of this section, it is pertinent to note that, while the use of pressure tanks for the storage of petroleum products has markedly reduced evaporation losses, it has also introduced maintenance problems. Larsen discusses the precautions to be observed to insure safe and efficient operation of all sizes of pressure storage vessels designed for working pressures ranging from 2.5 to 30 pounds per square inch. The Horton-Sphere is another type of storage vessel particularly suitable for the storage of volatile petroleum products such as gasoline or liquefied petroleum gases. Britton and Brinton report on the evaporation losses from gasoline storage tanks maintained under about 13 inches of water pressure. The loss from these tanks was 0.21%, as compared with 2% for tanks operated at atmospheric pressure over a period of a year.

Briers and Glanville have patented a storage tank for petroleum oils or other volatile liquids, the main feature of which is a float, slightly smaller than the tank diameter. In this manner the surface of the liquid subject to evaporation is greatly reduced.

The use of floating tops for petroleum and petroleum products storage tanks has increased, because of the advantages offered by such an arrangement. The floating top rises and falls with the expansion of the liquid in the tank, the tendency of the gasoline or oil to vaporize is checked, and the fire hazard has been reduced. Schmidt and Szczepanski have described those floating tops for storage tanks and have discussed their advantages as indicated above. Patents have been
granted to Bohnhardt(25), Carney(26), and Higgins(27, 28, 29) on tanks with a floating roof, and to Staber(30) and Runge(31) on tanks with a superimposed tank to permit the expansion of the liquid in the main tank without a vapor space developing in the tank. Hill(32) has patented a tank with cover and condenser arrangement to minimize vapor loss.

It is recognized that petroleum oils become viscous or even solid at low temperatures. Most tanks for the storage of such materials are provided with heating coils of some type, in order to keep the material at a temperature that it can be pumped. Even though this appears simple and obvious, some patents have been granted on storage tanks provided with heating coils. The patent granted to Stockdale(33) is an example of such an arrangement.

Storage in Concrete Reservoirs

In some sections of the United States, particularly in California, steel was not produced locally, but was shipped in by rail or boat from midwestern or eastern producers. Shortages and slow deliveries were regular, and, in an effort to find a satisfactory material of construction, attention was turned to the use of concrete. This material could be readily handled and attempts were made to produce satisfactory storage vessels for petroleum and petroleum products. At first the main difficulties experienced were connected with the production of a uniform, dense concrete mixture in order to prevent leakage. Later, surface treatment of the concrete and the use of admixtures insured satisfactory tanks.
Arey\(^{(34)}\) reports on the use of concrete for oil reservoirs in the southwestern part of the United States for storing asphalt-base oils. The results obtained were fairly satisfactory, but it was observed that the oil would sometimes penetrate into the walls of the tank for a distance of approximately \(1\frac{1}{2}\) inches. In 1914 the largest oil storage tank of its kind east of the Rocky Mountains was constructed of concrete at Gainesville, Texas. Brief details of the design and construction of this oil storage reservoir of 375,000-barrels capacity indicate the possibilities of concrete in tank construction\(^{(35)}\).

Freeman\(^{(36)}\) claims that if a concrete tank is carefully built, allowed to dry properly, and given a coating of rich cement, it will be impervious to light oils of low specific gravity. Sometimes a coating of sodium silicate is necessary to seal the pores of the concrete in order to achieve an oil-tight tank. Over eight years of experience with this type of reservoir have shown these tanks to be entirely satisfactory containers for California crude oils.

Andrews\(^{(37)}\) gives specifications for the construction of concrete oil-storage reservoirs which have proven successful in use. He recommends coating the interior of the tanks with sodium silicate to seal the pores of the concrete. The Standard Oil Company at Al Segundo, California, has built concrete oil storage reservoirs directly upon the ground, using four inches of concrete reinforced with 6 in. x 6 in. wire reinforcing for the walls\(^{(38)}\). No expansion joints were employed, and the results obtained have been quite satisfactory. The Westinghouse Electric Company at its Trafford City, Pennsylvania, plant employs three concrete tanks 37 feet in diameter and of 125,000-gallons capacity for the storage of fuel oil. A concrete hardener was used on the cement.
surfaces of the tanks. Based on its experience, this company recommends the use of high-grade cement and the continuous pouring of cement to obtain a monolithic wall for the prevention of seepage of oil from the finished tank (39). An article appearing in an oil trade magazine in 1922 (40) presents a list of companies, the number and capacity of oil storage reservoirs used, the date of construction, the gravity of oil stored therein, and kind of treatment, if any, applied to the tank.

Baker (41), reporting on new uses for cement in oil storage, describes the construction of concrete oil storage tanks, and emphasizes the precaution that must be observed in order to obtain a satisfactory tank. Hough (42) gives practical information on water-cement ratios. For reservoirs intended for the storage of low-sulfur crude oils, approximately $5\frac{1}{2}$ to 6 gallons of water should be used per sack of cement; for high-sulfur crude oils, the water should be reduced to 5 to $5\frac{1}{2}$ gallons per sack of cement. The cement must be carefully cured for 7 to 10 days by sprinkling or inundating with water, in order to assure a strong cement structure.

Berthelot (43) discusses the advantages of metallic and concrete reservoirs for storing hydrocarbon oils. Losses by evaporation and costs are compared.

Host (44) describes the construction of a concrete benzine storage reservoir built under the water.

Recent articles by Boase (45) and Collier (46) stress that the steel shortage has led to the development of concrete oil storage reservoirs, some of which have been constructed under the ground. These underground reservoirs are claimed to reduce evaporation losses tremendously.
Shepard(47), Garrabrant(48), and Hadley(49) describe the construction of concrete storage tanks employing prestressed design to minimize shrinkage and cracking. These tanks are used for the storage of aviation gasoline, fuel, and Diesel oils. Centrifugally cast and vibrated concrete oil storage tanks have also been described(50).

Combination of steel and concrete construction have also been utilized. The tank patented by McNeil(51) is an example of this type of construction.

**Linings for Concrete Oil Storage Reservoirs**

As mentioned previously, the use of various types of linings for storage reservoirs is necessary to prevent the seepage of the petroleum, petroleum products, or other oils into the concrete. The structure of concrete is essentially porous and great care must be exercised during construction of the tank to reduce the porosity to a minimum. One of the oldest methods used to make cement waterproof and dense is to incorporate a small amount of hydrated lime in the mixture. Other methods utilized a very dense finish coat of neat cement. Cements that are relatively waterproof have been available for some time, "Medusa" cement being one prominent brand(52), and these cements are used in the concrete mixture and as a finishing coat. Stuart(53) suggests the use of a waterproof pozzolana cement made oilproof by the Sika-Francois process. The Sika-Francois process is rather obscure. However, Rudzich(54) indicates that "Sika", a colloidal solution of light and heavy metals, is used as a paint for rendering concrete proof against oils. Further references to water and oilproofing materials developed by the Francois Cementation Co.,
L Ltd., indicates that dispersions of clays and bitumens, and sodium silicate, sodium carbonate, and other solutions are employed to render concrete waterproof and oilproof (55, 56).

Grigor'ev and Bargteil (57) describe coatings for rendering concrete tanks impervious to oil or water. One of these coatings is composed of varnish, lime, and clay and the other is composed of cement, clay, sodium fluosilicate, and sodium silicate (water glass) solution. The concrete tanks are coated with these coatings and permitted to dry or cure before oil is stored in them.

It is claimed that concrete may be rendered impermeable to mineral oil by applying to the concrete surfaces a hot mixture of gelatin glue (1 part in 4 parts water) and glycerol (0.1 part), and then fixing the coating with a formaldehyde solution (58).

Pearson (59) describes a method of testing coatings for concrete gasoline storage tanks. Small concrete containers treated with the coating material and samples of gasoline are stored in these containers. Visual examination and determination of loss of gasoline by weighing at periodic intervals is used to evaluate these coatings. Test results are given, but the coatings used are not identified.

Natural and synthetic rubbers have been used alone in combination to line oil storage reservoirs, in order to prevent losses by seepage and corrosion of the container. Cleghorn (60) has proposed the use of a sponge rubber lining coated with Turkish bird-lime. Such a coating is claimed to prevent corrosion of the container. Macbeth (61) utilizes an inner layer of oil-impermeable material, such as gum lac, and
an outer "self-sealing" material, such as unvulcanized gum rubber held between two sheets of vulcanized rubber compound.

Pryor(62) discusses the physical and chemical properties of Neoprene and its applications in the petroleum industry. Neoprene is unlike natural rubbers in that when in contact with petroleum oils it does not deteriorate to the same extent. Natural rubber on contact with petroleum distillates will swell, and as it swells there is a tremendous decrease in tensile strength, toughness, and abrasion resistance. Neoprene is of particular interest to the petroleum industry, because of its resistance to swelling and also because of its resistance to oxidation, sunlight, heat, and chemicals. This article by Pryor illustrates the utility of Neoprene in the petroleum industry by presenting a table showing the relative swelling of Neoprene and rubber. With all oils used in these tests, Neoprene was considerably better.

Taylor(63) reports that prestressed concrete storage tanks lined with Thiokol synthetic latex have been found very satisfactory for the storage of gasoline. The method of lining tanks with Thiokol latex is claimed to be very flexible under different conditions(64). This Thiokol lining is applied like wallpaper. A rubber cement is first applied to the storage tank and the solvent is permitted to evaporate until the proper degree of tackiness has been reached. At this stage the sheets of Thiokol are set in place and they adhere instantly(65).

Crosby(65) claims that this type of lining protects the fuel from alkalis present in the concrete, thus preserving high octane qualities, as well as preventing loss by seepage. Other articles by Taylor(66) and Spamer(67) relate the experiences of the U. S. Navy, Bureau of Yards and
Docks, in the application of Thiokol and other protective linings for concrete storage tanks for aviation gasoline, Diesel fuels and fuel oils.

Taylor(63, 66) describes the use of synthetic resin linings for sealing the pores of concrete oil storage reservoirs. These synthetic linings are applied by spray gun and dried, sometimes by the use of infrared lamps. Other resin linings which have been employed include Heresite(68), Lithcote(69), and Havey(70).

**Linings for Steel Storage Tanks**

Crude petroleum often has a very corrosive action on steel storage tanks, due to the presence of sulfur compounds, water, and dissolved salts. This corrosive action has been very severe in some instances and has caused the collapse of the tank roofs and even the tanks themselves.

Some of the so-called "sour crudes" contain sulfur compounds which, on handling and transportation, evolve hydrogen sulfide. The hydrogen sulfide reacts very readily with iron to form iron sulfide in an extremely active form, the reaction product often catching fire on exposure to the air. The danger from fire and to health is a real one, and every method is tried to combat corrosion due to these sulfur compounds.

In order to reduce the corrosion of steel tanks, many types of surface coatings have been tried. Ballard(71) proposes the use of sprayed zinc and zinc chromate coatings on the interior of gasoline tanks. These coatings have proven fairly satisfactory in use, but there is always the danger of contamination of the gasoline by particles of zinc compounds which might form and slough off. Pessel(72) reports that
sprayed cadmium coatings are better than those of sprayed zinc. A considerable reduction in the amount of sludge collecting in the bottom of the tank was noted when gasoline stored in cadmium-coated tanks was compared with that stored in zinc-coated tanks. Coatings of sprayed aluminum have also been tried. Some degree of success has been obtained, but incomplete coverage of the steel base metal is the one disadvantage of such coating with aluminum. Thin aluminum sheet attached to the steel tank has also been tried. While aluminum successfully resists the action of hydrogen sulfide, the greatest disadvantage with using aluminum sheet is that no really good adhesives for cementing the two materials together have been found.

Many types of paints and lacquers have been tried and some of them have shown some promise. Mead has offered tentative specifications for protective coatings for petroleum storage tanks, and these specifications are as follows:

1. The material must be suitable for spray application.
2. Poisonous vehicles, solvents, and pigments must be absent.
3. Drying must take place rapidly.
4. Heat treatment must not be necessary for hardening the coating.
5. The coating must bond well to steel.
6. The coating must be cheap.
7. The color should be light, in order to facilitate observation of the progress of the paint job.
8. The coating must be unaffected by water and water vapor, steam, and hydrocarbons in either liquid or vapor form.
9. The coating must resist attack by hydrogen sulfide.
10. The coating must resist excessive temperature changes.

11. The coating must be unaffected by exposure to air.

Perry(74) emphasizes the fact that the use of noncorrosive metals and alloys are expensive, and that paints, while not satisfactory in every sense of the word, are reasonable in price and, with proper precautions, do give good service.

The use of a coal tar-pitch-asbestos admixture has been suggested as a corrosion-preventive lining(75). This type of lining has some advantages, but corrosion is known to proceed under such coatings, if the surface was not entirely dry when the coating was applied.

Miscellaneous Tanks for Storage of Petroleum Products

Schmidt, Devine, and Wilhelm(76) have investigated the use of aluminum for the construction of petroleum storage tanks and find that this metal has great possibilities, because of its resistance to corrosion by hydrogen sulfide. Certain precautions, however, must be observed in the operation and maintenance of these tanks. In order to obtain satisfactory life from tanks fitted with aluminum steam coils, the steam coils must not be permitted to come in contact with salt water. Concentrated brines do cause corrosion of aluminum tanks, and every effort must be exerted to drain off any brine layer that may accumulate. Electrochemical corrosion sometimes develops when iron and aluminum are used together, if electrolytes are present. Dix and Mears(77) have investigated causes of corrosion of aluminum aircraft fuel tanks, and they find that corrosion of these tanks is due solely to the presence of water contaminated with heavy metal salts. Troubles due to corrosion can be overcome by designing tanks to permit drainage of water, selecting
metals to avoid electrolytic action, and handling the fuel so that it will not pick up water, iron rust, or other heavy metal corrosion products prior to the time it is pumped into the aircraft fuel tank. The use of suitable paints is also recommended. A paint comprised of zinc chromate pigment and phenolic resin vehicle possesses good adherence and does not dissolve appreciably in the fuel. The use of corrosion inhibitors such as sodium chromate is also recommended to prevent corrosion.

**Losses of Petroleum and Petroleum Products Due to Evaporation**

By far the greatest number of storage tanks for petroleum and petroleum products are constructed above the ground and are wholly unprotected from the action of the sun, wind, rain, and snow. Such an arrangement is usually necessary because of safety regulations. The petroleum producers and refiners have long recognized the fact that tremendous quantities of petroleum products are lost by evaporation, especially during hot and windy weather, and they have made a tremendous effort to reduce these losses. The "breathing" of storage tanks, due to expansion of the contents on heating and contraction on cooling, results in a loss of product on the one hand and the introduction of moisture on the other hand, unless the tanks are provided with specially designed vents and systems designed to adsorb and recover the products normally lost. It is recognized that temperatures within the storage tanks are lower when the tanks are painted with light-colored paints than when dark paints are used. This is due to the absorption of light and heat rays to a greater extent by dark paints than by light-colored ones, which reflect the light and heat rays. Insulation has been used to maintain
even temperatures in the storage tanks and thus cut down evaporation losses. Discussion of these methods follows.

Dowie(15) surveys the general practices in the petroleum industry and finds that many methods of reducing evaporation losses are employed. The use of tanks provided with water-seal tops and sprinkling the top and walls of the tank with water has helped to keep the contents of the tank cool and reduce vaporization. The use of insulating materials and the encasing of the tanks in a tile case, also been tried. Dowie also recommends that the tanks be painted a light color, preferably white, in order to decrease losses of petroleum products in storage.

Schmidt and Wilhelm(78) also investigated the effect of color of paint used on gasoline storage tanks. Their findings are similar to those of Dowie(15). They found that in a series of tanks used for gasoline storage, one of which was painted with white paint and provided with an insulated roof, another painted with red iron oxide paint, a third painted with aluminum paint, and a fourth covered with aluminum foil 0.001 inch thick attached to the steel shell by means of an adhesive, that the losses were least from the first-mentioned tank and greatest from the tank coated with red iron oxide paint. The temperatures of the gasoline stored in the tanks were greatest in the tank coated with iron oxide paint and least in the tank painted white. The maximum temperature observed during the thirty-day test period was 148°F. in the red iron oxide-coated tank. Other factors which influence evaporation include maintenance of the tank under pressure and the methods of filling. The practice of bottom-filling is recommended. The work of Deacon(79) corroborates the results of Schmidt and Wilhelm.
Arend\(^{(60)}\), in discussing evaporation losses from oil storage tanks, claims that the loss of product from a conical roof tank is 1.94 times greater than the loss from a similar tank provided with a water spray. Arend also states that vermiculite has been used with some success in place of asbestos for tank insulation.

The use of floating tops, such as those patented by Wiggin\(^{(27, 28, 29)}\), in the petroleum industry has helped considerably to reduce losses by evaporation. These tops rise and fall with the expansion and contraction of the contents of the tank, and breathing losses are largely eliminated, because there is no vapor space due to the top resting directly on the surface of the liquid. Wiggin has also patented a breather roof which expands to take care of the increased volume of vapors. A pressure relief valve permits the vapors to escape if the volume of vapors generated exceeds the capacity of the roof\(^{(81)}\). Carney\(^{(25)}\) has also devised a storage tank with floatable diaphragm, which has been used to some extent.

The use of vapor-tight tanks is one method of reducing vapor losses. Wiggins\(^{(82)}\), writing in 1922, states that the loss from the evaporation of crude oil produced in the United States in 1922 had a value of $250,000,000. He claims that most of this loss could have been prevented by using vapor-tight storage tanks. In one series of tests it was found that the percentage loss of product from tanks having a four-inch vent was 1.21% and only 0.26% from a vapor-tight tank. Britton and Brinton\(^{(21)}\) state that gasoline storage tanks maintained under about 13 inches of water pressure showed an average evaporation loss of 0.21% over a period of one year, as compared with a loss of 2% from tanks.
maintained at atmospheric pressure. Schmidt and Wilhelm\(^{(83)}\) state that approximately 1.5% of the motor fuel in bulk storage is lost by evaporation, and that this loss can be reduced by at least 50% by (1) the use of vapor-tight tanks, (2) use of floating tops, (3) by maintaining the storage tanks under high enough pressure to prevent breathing losses, and (4) by installing vapor-recovery equipment. In addition to these four methods, the use of light-colored paints, insulation, and under-surface loading all help to reduce losses due to evaporation. Ashley\(^{(34)}\) has found that certain factors must be considered in any study of losses of product by evaporation during storage. Of these, the vapor pressure of the oil, the oil surface temperature, average oil temperature, weather conditions, size of tank, kind of tank roof, pressure regulation in tanks, color of paint, and volume of oil being stored have a profound bearing on losses. In this connection the Reid vapor pressure of the material being stored may be used to determine the proper storage tank pressures.

Several systems have been devised to minimize breathing losses. One of these systems employs compression. The vapors emanating from the storage tanks are collected in accumulators and then are compressed to the desired pressure and passed through condensers where condensation to a liquid takes place. The liquid is returned to storage and the noncondensed vapors may be bled off or passed to an absorption system. The vapors may be passed through an absorber employing a scrubbing oil, and the gasoline or other products recovered by steam distillation. This system is usually referred to as the absorption recovery system. A third system employs an adsorbent. Siebert and Gregg\(^{(85)}\) have patented
a process in which the vapors are passed through an adsorber containing activated charcoal or silica gel. Wilson \(^{(86, 87)}\) has patented a similar arrangement employing adsorbent materials. In order to prevent oxygen from being introduced into the tank, Harnsberger \(^{(88)}\) proposes using a device through which a liquid such as pyrogallic acid solution may be circulated.

The use of breather bags is widespread. Halbert \(^{(89)}\) describes an installation in which the vents from the storage tanks are connected to a breather bag, fabricated from cotton fabric impregnated with a glue-glycerol mixture, as the temperatures in the storage tank increase, the breather bag is expanded. On cooling, the pressure in the tank drops and the breather bag contracts. No vapors are lost, but a considerable amount of vapors are present in the circulating system. By the use of such a system, the loss due to evaporation was reduced to 0.04%. Wilson, Brown, Atwell, and Chenicek \(^{(90)}\) describe this system further, and give considerable information on the construction and use of the bags. They recommend that the breather bags be installed in a building or tank where they will not come in contact with water, for these devices, while oil-proof, are not waterproof. Information on the costs and savings of an installation are given, but these data are of little value at the present time. Other applications for breather bag installation for crude oil and other light oil storage are discussed. Wilson \(^{(91)}\) has patented an arrangement of equipment comprising storage tanks and breather bags impervious to petroleum oil vapors.

As an outgrowth of the breather bag system, Bignoll \(^{(92)}\) discusses the use of steel balloons for the same purpose.
McGrath(93), in discussing the various methods for reducing vapor losses from storage tanks, lists five different methods by which a reduction of losses may be accomplished. These methods include:

1. Vapor-tight containers covered with a light-reflecting paint.
2. The use of a breather-roof or balloon-roof on normally full tanks.
3. The use of a breather-bag system.
4. Floating roofs on tanks that are filled and emptied frequently.
5. The use of pressure containers.

His recommendations follow the customary practices of the industry.

Insulation of the tanks has helped considerably to reduce evaporation losses. The use of insulating materials has been discussed by Dowie(15), Schmidt and Wilhelm(78, 83), Arend(80), Britton and Brinton(21), Palei(94), and Stefanor(95). Asbestos, magnesia, vermiculite, felt, and gypsum are some of the insulating materials that have been employed. They are usually covered with a waterproof covering and painted in light colors. General application of insulation is on the top of the tank to prevent vaporization of the contents.

The use of foam on the surface of the petroleum or petroleum distillate has been used to prevent losses by evaporation. "Sealite" is a foam which has been used for this purpose. This material is composed of cornstarch, glycerol, gelatin, and other ingredients, and about 50% air floats on the surface of the oil. It has good stability, except in humid climates where the absorption of water tends to break the foam(90,
This foam appears to have some fire-protective qualities\(^{(96)}\). Porter\(^{(97)}\) claims that there was no difference in the evaporation loss when "Sealite" was used, in comparison with a vapor-tight tank in a one-year service test. These tests also indicated that "Sealite" could not be depended upon to be stable over this period of time. Patents granted to Jennings\(^{(98, 99, 100)}\) and to Howard, Kent, and Jennings\(^{(101)}\) cover the use of a foam similar to "Sealite" referred to above.

A final method of reducing evaporation losses is to construct the tanks in the ground or below the surface of the ground. This method was particularly useful in military operations where losses were reduced and a natural camouflage was had at the same time\(^{(102)}\).

**Safety and Fire Protection**

The petroleum refiners have been leaders in the application of safety and fire protection, and they have discarded practices found unsafe. A committee of the American Petroleum Institute regularly studies the causes of fires in the industry, and their findings and recommendations have led to a vigorous training program within the various companies. The U. S. Bureau of Mines has been active in this work also, and many bulletins, technical papers, and reports of investigation have been published which contain valuable information on hazards, explosive limits of petroleum hydrocarbons and gases, and permissible devices for use in the industry.

It is the general practice in the industry to "ground" all tanks, so that danger from lightning and static electricity will be minimized. Various lightning protective systems have been devised, and
these systems include a number of sharp metallic points extending into the air and "grounded" through a heavy copper conductor.

The danger from fire is ever present in petroleum storage and petroleum refining operations. Fires may be caused by explosions of mixtures of the oils with air, by "boil-overs", leaks, spontaneous combustion, and from lightning and static electricity. Williams-Gardner (103) investigated the atmospheres in storage and process tanks and found no explosive mixtures to be present. The greatest danger from explosive mixtures would occur when tanks are drained or at a time when the excess pressures within a tank were vented. Since most vents are provided with safety screens and flash-back arrestors, there is less danger from this source than is commonly supposed. The use of nitrogen, carbon dioxide, or mixtures of the two (inert gas) is often used to reduce the tendency to form explosive mixtures (104).

The control and extinction of fires in petroleum storage and operating vessels is usually accomplished first in the design and layout of the installation, and secondly by the use of steam or "Foamite" solutions. Every precaution to prevent fires from lightning and static is incorporated into the plant design. The designer has also incorporated into the plant design an adequate system of steam distribution and Foamite distribution available for use in emergencies. The most reliable method of extinguishing fires involves the rapid application of a foam on the oil surface, which shuts off the air from the oil and stops the combustion. This foam is caused by the interaction of an acid solution, consisting of aluminum sulfate in water, with an alkaline solution consisting of sodium carbonate, water, and a froth-forming agent such as
licorice or saponin. On mixing equal volumes of these solutions a foam, equal to approximately six to eight times the volume of the combined solutions, is formed.

From time to time, various bulletins on fire prevention and safety have been issued by the U. S. Bureau of Mines, American Petroleum Institute, National Fire Protection Association, Underwriters Laboratories, and the Associated Factory Mutual Insurance Companies. The lists of these publications are available from these organizations on application.

ORDNANCE DEPARTMENT: REQUIREMENTS FOR THE STORAGE OF PETROLEUM OILS AND MATÉRIEL IN PETROLEUM OILS

As has been stated in the introduction of this report, it is the aim of the Ordnance Department of the U. S. Army to maintain a supply of ordnance matériel in comparative readiness for use over a long period of time, such as fifty years. Of the various methods of storage, consideration is given in this report to the storage of petroleum and petroleum products, and to the storage of ordnance matériel in an oil medium. Outside of the general conditions of storage of petroleum and petroleum products, which are discussed in the preceding section, there are specific requirements for the storage of ordnance matériel, and these will be discussed in this section. Following sections will cover changes which occur in the oil over a long period of storage and use, and changes which might occur in the different pieces of equipment due to action of the oil.
The general conditions of long-term storage have been set forth in a tentative specification\(^{(105, 106)}\). The length of time has been set as fifty years. Temperatures may vary from as low as \(-60^\circ F\) to as high as \(170^\circ F\), for prolonged periods, and the seasoned variation may be within these limits. Humidity will vary, depending on the location and temperature. The containers which might be used range from small cans to large tanks, and these may be constructed from a wide variety of metals or of concrete.

Ordnance materiel may be stored complete or disassembled. A list of the types of equipment which is to be stored in experimental studies has been compiled\(^{(107)}\), and the conditions of storage have been indicated. No particular details were given, as these were to be worked out by others. Some further indications as to the progress of this experimental program are given in a communication\(^{(108)}\), which supplies data on contracts that have been placed. Some of this equipment is to be stored in oil where possible. A list of vehicles which would have to be stored has also been prepared\(^{(109)}\).

Certain requirements for the containers used in storing equipment have been formulated\(^{(110)}\). These requirements were as follows.

a. The container shall be capable of being hermetically sealed and be leakproof both from diffusion and actual leakage around joints.

b. It shall be of such a design as to permit the maximum possible density of items in the package.

c. The materials used in the manufacture of the container assembly shall be of such composition, or so protected, as
to last for a period of fifty years actual storage in the open and internally will not be affected by the storage media.

d. The supporting media for items within the package shall be placed in such a manner so as to provide maximum protection for the container assembly and the item stored.

e. The container will be so designed as to assure ease of complete removal of residual air and moisture.

f. The container will be designed in such a manner as to withstand pressure changes.

g. The container will be designed as to be readily opened by facilities at hand.

h. The container will be designed in such a manner that storage media may be changed or replaced by either gas or liquid.

i. Containers or container will be so marked that the contents will be known, and the marking media must withstand the same conditions as the container proper.

j. Container tops will be designed not to trap water.

k. Container will be designed for stackability and palletized handling.

l. Containers for both individual and multiple packaging will be developed.

These requirements have been studied by several industrial organizations cooperating in this work, and preliminary results are described in an Ordnance Department publication. Further work on the development of containers has been conducted by The International Harves-
ter Company, Erie Proving Grounds, and Frankford Arsenal. Their various reports pertaining to this program should be consulted for details of the developments. The report by Mueller\(^{111}\) contains much information on standard and extended drum containers. The sealing of the drums presented the greatest problem, but the method evolved withstood the tests for leakproofness, resistance to rough handling, and temperature changes. This method consisted of soldering in a protective inner bulkhead under the regular cover. The space between the inner cover and the outer cover is then filled with asphalt to avoid an air pocket.

While the above type of construction is satisfactory for small containers, it would not be suitable for large containers, such as 50,000-barrel oil storage tanks.

There are several factors which must be considered in a program involving the storage of Ordnance materiel in oil\(^{112}\). These are evident, and are mentioned in several of the reports mentioned heretofore.

a. Space requirements for large-size and smaller containers.
b. Volume of oil required for immersion of equipment.
c. Disassembly of individual pieces of equipment. A disassembled gun cannot come out fighting.
d. Cost of oil, containers, and preparation for storage.
e. Danger from fire is ever present.
f. Long-term stability of oils for storage is unknown.

Some preliminary information is available on the cost of packaging small arms for long-time storage in an oil medium in hermetically sealed containers\(^{113}\). The number of pieces of material to be stored is
13,531,075. The ground area required will be \(18\frac{1}{2}\) acres. Cost of containers, based on the use of standard 16-gauge 55-gallon drums, is $5.75 per container, freight included.

Cost of packing container, including oil, labor, heat, light, and power is $23.00 per container. Cost of palletizing will average $28.20. Cost of asphaltic coat on container and pallet is $2.00 per container. Cost of one container stored in the field is $38.95, and average weighted cost per item of all small arms materiel is $1.18. Total number of containers used will be 400,000.

In this program 12,000,000 gallons of oil will be required.

The question of atmosphere above the oil in large containers is one of great importance. Oxidation reactions will take place, even though the temperatures are kept within the range previously mentioned. One manufacturing company maintains an atmosphere of nitrogen over the oil in the electrical transformers, and has found that if the oxygen content of the gas above the oil is kept below 0.1% there is no oxidation or contamination of the oil (\(11b\)). The breather pipes of the transformers are connected to a chamber which contains a deoxidizing agent. The use of a "breather bag" system in connection with an inert gas supply appears to be applicable to large tanks used in long-term storage operations.

Information pertaining to the oxidation of oils will be discussed in a later section of this report.
OXIDATION OF PETROLEUM OILS

General

In making a literature survey of the oxidation of petroleum oils with the object of predicting their oxidation behavior in long-term storage, practically nothing can be found of an experimental nature that pertains directly to changes occurring during storage. However, there is an extensive literature reporting the deterioration of oil under conditions more drastic than those found in storage or use of the oils, in order to foretell their fate in long-term use in transformers, turbines, and other equipment.

The criteria of deterioration of oil usually taken are increase of acidity of the oil and precipitation of sludge from it. The studies reported in the literature imply that deterioration is caused by atmospheric oxidation, which results in the formation of peroxides, alcohols, aldehydes, ketones, and acids. The phenomena of autoxidation are attributed to the formation of peroxides. Aldehydes and ketones are known to react by condensation to give high-molecular weight compounds which are not very soluble in oil. The formation of acids causes corrosion of metals, producing soaps of limited solubility in oil. The oil-air reaction is catalyzed by metals, their oxides, and soaps. Polymerization is eliminated as a cause of deterioration if an oil is properly refined and not subjected to cracking by heating to elevated temperatures.

Considerable work has been done to inhibit the oxidation of oils by addition of antioxidants, which increase the induction period of
the reaction and thus prolongs the stability of oil in storage. This subject will be discussed in a separate section.

**Determination of Oxidation Stability**

Resistance to oxidation is considered a very important characteristic of an oil. Stability of the oil is measured by various tests, such as the Indiana Oxidation Test for Motor Oils, Sligh Test, Brown-Boveri Transformer Oil Test, and the German Tar Number Test. It has been pointed out by Kalichevsky that none of these tests guarantees the perfect performance of an oil in service. Likewise, it is not infrequent that the results obtained with one test are in contradiction with those obtained by another. When the conditions of the test are made to coincide with the service conditions, agreement is better between the test results and the performance of the oil in service. In several of the tests, metals are added which normally would come in contact with the oil, and, in these tests, the results are more closely in agreement with the service behavior of the oil.

**Mechanism and Theory of Oxidation Phenomena**

The mechanism and theory of oxidation phenomena have been studied by many workers. The Wieland Theory interprets the oxidation of petroleum in air as an indirect oxidation or dehydrogenation. An oxidation mechanism of paraffin hydrocarbons has been postulated by Egloff, Schaad, and Lowry. Dornte and Ferguson have shown that the oxidation of some white lubricating oils is not affected by the non-volatile oxidation products. No peroxides are formed, and water and
carbon dioxide are the principal products. The reaction is catalyzed by copper, iron, tin, and lead. In the case of copper, the rate increases greatly with the copper-oil ratio, while for the other metals this ratio has only a slight effect. In another study, Doernte, Ferguson, and Haskins (123) have reported an oil oxidation in which the reaction is apparently retarded by the products. E. L. Lederer (124) has made an extended study on the reaction kinetics of catalytic oxidation of hydrocarbons, which is useful in the study of transformer oils and lubricants.

A series of articles on the oxidation mechanism of mineral oils was reported by Teikichi Yamada. In the first article, a study is reported of the effect of moisture (125). He showed that white oil, when subjected to oxidation in the absence of a dehydrating agent, gave more acidic material. This observation was confirmed when the oil was oxidized in open and closed vessels at 120°C. with and without the following dehydrating agents: calcium chloride, sulfuric acid, phosphorous pentoxide, and potassium hydroxide. In another study, Yamada concluded that the oxidation of refined mineral oil is accelerated by the addition of organic acids (126). Yamada investigated the effect of alcohols, esters, and ketones (127) on the oxidation of white oil and switch oil at 100°C, by measuring the increase in oxygen pressure. The higher alcohols and ketones accelerated the oxidation. Yamada concluded from this that alcohols are primary oxidation products, but that they do not act directly as active centers. In the concluding paper in this series (128), Yamada reported on peroxide formation in the oxidation of mineral oil. Parallel determinations of peroxide value, acetyl value, and saponification number were made on samples of white oil oxidized in air for various lengths of time at 120°C. It was shown that the peroxide value passes
through a maximum and decreases before the maximum value of the acetyl value is reached. Oils containing the largest amounts of peroxides absorb oxygen most rapidly. In determining the peroxide values, Yamada used a modified Wheeler method in that ethyl alcohol was substituted for acetic acid as the solvent. The end-point was permanent in this solvent mixture; however, four to five hours were required for complete liberation of iodine, and therefore, lower peroxide values were obtained.

Kreulen and ter Horst\(^{129}\) investigated the rate of reaction in the system mineral oil-oxygen and the mechanism of the influence of copper and tin on this system. In this work, it was shown that mineral oil, when vigorously stirred with oxygen at 150°, slowly undergoes oxidation to acids, ketones, and other oxygenated compounds. The over-all oxidation rate is followed by the determination of the dipole moment of the oil. A long induction period, greatly decreased by the addition of finely divided copper and tin, was observed. The authors believed that this induction period was due to the presence in the oil of antioxidants, which are removed by adsorption on copper and tin. Copper is a better adsorbent and reduces the induction period much more than tin.

The mechanism and oxidation of mineral oils are discussed by Mead and Collaborators\(^{130}\) employing a static method and by Haslam and Frolich\(^{131}\) by a dynamic method.

**Solubility of Oxygen in Mineral Oils**

The solubility of oxygen in mineral oils was determined by Maillard, Vellinger, and Verdier\(^{132}\). They found that about 12 cc. of oxygen dissolved in 100 cc. of oil at 20° and 760 mm. of pressure,
regardless apparently of the origin of the oil. The oxidizability of the oil is influenced by the degree of refining, according to these authors. Gemant (133) made measurements of air absorption by various oils at room temperature and by noting the solubility change at 80°C, showed an independence of the absorption coefficient within 1% in this range. The Bunsen coefficient varied from 0.073 to 0.106, decreasing with increasing oil viscosity.

**Oxidation of Oil by Air**

The behavior of high-boiling mineral oils on heating in air was investigated by C. E. Waters (134). In these oils so-called asphalts insoluble in petroleum ether were formed in amounts depending on the form of the vessel used, and the material of which it is made.

Titunikoff (135) studied the oxidation of naphtha oils by air. His work indicated that oxidation was favored by rapid flow of air, higher temperatures and increased pressure. The use of 0.3% of a metallic oxide greatly increased the oxidation of the oil; manganic oxide, precipitated manganese dioxide, and lead oxide were most active in the order named. By long-continued passing of air, oxidation of 90% of the oil was obtained.

The atmospheric oxidation of paraffin was investigated by Grun and Ulbrich (136), who found that the yield of acids from paraffin by oxidation with a current of air at 160°C increased with the quantity of air and time of oxidation. They observed that traces of water in the air promoted the oxidation, while CO₂ in the air retarded the reaction.

In a study of transformer oils, J. O. Wilson (137) pointed out that air is an essential factor in the deterioration of oils, and,
therefore, a transformer should be designed to prevent "breathing" due to changes in temperature. Yamada\(^{(138)}\) emphasized the detrimental effect of air on oil in investigating transformer oil sludges. In this work, it was shown that transformer oils which produced sludges readily on heating with air did not form sludge when heated under vacuum, or in an atmosphere of carbon dioxide, nitrogen, or hydrogen. Westinghouse Manufacturing Company\(^{(139)}\) uses an atmosphere of nitrogen over oil in a transformer. In order to keep the oxygen content below 0.1%, the atmosphere in the transformer is attached to a breather arrangement to take care of temperature changes. The breather arrangement removes oxygen from the air, so that there will be no contamination or oxidation of the oil.

Experiments on the oxidation of mineral oils have been reported by Moore and Barrett\(^{(140)}\), Hicks-Brunn, et al\(^{(141)}\), Van Rysselberge\(^{(142)}\), and Chernozhukov and Krein\(^{(143)}\). It has been the general observation in all of this work that aging of oil is primarily caused by oxidation. Large increases in viscosity of the oil on oxidation were reported and asphalt and acidity formation were roughly parallel.

**Effect of Degree of Refining on Oxidation of Oil**

G. Muller\(^{(144)}\) measured the absorption of oxygen by various transformer oils at \(110^\circ\) during periods up to 500 hours. He studied the effect of degree of refining on the amount of oxidation and found that super-refined (white oils) absorbed the most oxygen, partially refined usually the least and slightly refined an intermediate amount. Addition of copper stearate as a catalyst had little effect on the super-refined oils, but increased the oxygen absorption of the partially refined oils.
Kalantar and Gurvich (145) found that under-refined or over-refined turbine oils developed acidity on oxidation. Butkov (146) reached the same conclusion earlier, and believed that the susceptibility to oxidation of refined oils was caused by removal of antioxidants on refining.

H. von der Heyden and K. Typke (147) found that the oxidation of highly refined oil was decreased by the addition of magnesia, magnesium carbonate, lead oxide, salicylic acid, hydroxylamine hydrochloride, and prevented by the addition of pyrogallal and aniline. The oxidation of oil is increased by the addition of sodium hydroxide, sodium carbonate, potassium carbonate, lead dioxide, phenol, oleic, and oxalic acids.

M. Muller (148) showed that refined oils absorb much more oxygen below 150°C than partially refined oils, but above 150°C the absorption was about the same for both oils.

M. V. Kurlin and I. M. Blinova (149) reported the more severe the original refining of the oil, the more unstable the oil is during use, and, accordingly, the more oxygen it absorbs. He concludes that so-called white oils should not be used in equipment where they are exposed to air.

S. J. M. Auld (150) showed that solvent-refined oils have much better characteristics than oils refined by conventional methods.

Blending experiments with different transformer oils by von der Heyden and Typke (151) showed that by mixing super-refined oils with less refined oils the properties of each were mitigated. H. H. Golde (152) demonstrated that no harmful effects resulted from mixing Russian oil with Pennsylvania or Texas oil, or the reverse.
H. Stäger(153) showed that if transformer oils are too highly refined, peroxides and volatile acids are formed, during the oxidation of the oil, which are destructive to textiles, lead, and cadmium.

**Effect of Addition Agents on Oxidation of Oil**

The oxidation of mineral oils by air and oxygen has been studied by a number of workers, with the objective of showing the harmful effect of materials that may come in contact with the oil, or to find inhibitors and antioxidants to retard oxidation. The following sections will discuss the work done on the effect of metals and their oxides and salts, as well as the inhibiting effect of organic compounds and sulfur.

**The Effect of the Presence of Metals and Their Salts on the Oxidation of Oil**

Evers and Schmidt have investigated the artificial aging of oil in the presence of catalysts(154, 155, 156, 157). They have expressed the aging curve by an equation which supposedly allows one to calculate the saponification value, acid value, and tendency to polymerize during various stages in aging.

Vellingor and Muller(158) found that the extent of air oxidation at 110°C of transformer oils was proportional to the time of heating and the amount of copper dissolved in the oil as cupric stearate. Copper metal, when suspended in the oil containing the copper, had no effect, becoming coated with an adsorbed layer of copper salts of the acids formed by the oxidation of the air.

The oxidation of oils was investigated by E. W. J. Mardles(159). He reported that sludge formation was inhibited by salts of tin, while
compounds of copper, iron, silver, vanadium, and manganese accelerate the rate of deterioration.

H. v. d. Heyden and Typke\textsuperscript{(160)} heated transformer oils with metals in the presence of excess air for 70 hours, but showed no change in acid number or tar number. In a later article, they reported\textsuperscript{(161)} that copper alone or in combination with other metals had an unfavorable effect upon the oil, while zinc or aluminum alone or with oxidized copper gave favorable results.

Farmer\textsuperscript{(162)} and Van Gils and Hagethorn\textsuperscript{(163)} reported on the action of metals on the oxidation of oil. Farmer showed that brass greatly accelerated the oxidation of turbine oil. Van Gils and Hagethorn observed that considerably more lead than copper was taken up by the oil. With copper no maximum in loss occurred, while in the case of the lead a maximum was determined.

Müller and Müller\textsuperscript{(164)} led air through lubricating oil for 8 hours at 95°C in the presence of different substances. The saponification number was not affected by metals, but was increased by metal oxides and metallic salts of fatty acids, and by agitation of oil. Water vapor and organic substances, especially resorcinol, pyrogallol, and other hydroxycompounds were inhibitors of the oxidation.

Clower and Clower\textsuperscript{(165)} studied the action of tin, lead, copper, aluminum, cast iron, steel, monel, brass, fine bearing metals, and lead-copper, lead-tin, and lead-steel combinations on turbine oils with and without inhibitors. The metals had less effect on the inhibited oil after heating for 200 hours at 275°F, but all oils were similarly affected after 600 hours at 275°F. The copper-lead combination had a
greater effect on the degradation of the oils than any single metal. The uninhibited oils were affected more by lead than any other single metal and copper was next in order. Bearing metal alloys did not affect the oxidation of the oil as much as did the individual metals from which they were alloyed.

Fr. Frank\(^{(166)}\) investigated the aging of lubricating oils by oxygen in the presence of the metals, lead, copper, iron, and other metals. He reported carbon monoxide and carbon dioxide among the oxidation products. Frank concluded that aging of lubricating oil is primarily due to oxygen and only incidentally to the metals.

Butkov\(^{(167)}\) explained the high oxidation of mineral oils by catalysis. Catalytic oxidizing agents can be metals, soaps, and organic compounds. The organic compounds behave as autoxidants. Butkov found that antioxidants such as B-naphthol and B-naphthylamine proved to be very effective.

C. E. Waters\(^{(168)}\) investigated the effect of various metals and metallic oxides on the carbonization values of two motor oils. Zinc and aluminum were found to be without effect under the conditions used. Steel, cast iron, nickel, and cobalt cause a small increase, while phosphor bronze, brass, and copper cause the oils to have a distinctly higher carbonization value. Copper oxide, nickel oxide, cobalt oxide, and ferric oxide were active, also. The greatest increases were obtained by exposing the oils to air and light for twenty hours before testing them.
Effect of Soaps and Acids on the Oxidation of Oil

The effect of various soaps in oil on the oxidation of oil was reported by v. d. Heyden and Typke (169) and Yamada (170). Copper stearate exerted a detrimental effect on oil while tin naphthenate prevents sludge formation in highly refined transformer oils. Yamada (171) showed that organic acids, such as stearic, oleic, naphthenic, and benzoic acids, accelerated the oxidation of highly refined mineral oil. While alcohols had no marked effect on the oxidation of highly refined oil, they showed a slight retarding action on the oxidation of less refined oils.

Effect of Inhibitors in Oil on the Oxidation of Oil

Jan Kryspin (172) oxidized samples of transformer oils by passing a slow current of oxygen through the oil for 60 hours at 120-122°. He added pyrogallol, a-naphthol, and meta-cresol (0.1 g. per 30 g. of oil) to determine the effect of phenols in preventing oxidation. The amounts of resins and asphalts resulting from the oxidation showed that these compounds did not exhibit any protective action on mineral oils.

A study was made of antioxidizing agents in oxidation tests on Rumanian transformer oils by Canda and Cristodulo (173). They reported that antioxidizing agents reduce the amount of peroxides and acids formed in the oxidation of oil.

The influence of sulfur on the oxidation of less refined transformer oils was studied by Mizushima and Yamada (174). An accumulation of sulfur was found in the sludge. They propose the use of sulfur to
hinder acid formation on oxidation. The same authors (175) added a slight portion of sulfur amounting to 0.1% to white transformer oil and tested the oil by oxidation for 100 hours under 86 cm. mercury pressure at 120°C. A parallel test without sulfur was carried out. The oil without sulfur oxidized readily, but the oil with sulfur added did not oxidize appreciably. Alkyl sulfides and mercaptans when added to the oil gave the same antioxidation effect, but thiophene did not inhibit oxidation. The authors concluded that the stability to oxygen of oils not highly refined must be attributed to the influence of sulfur compounds contained in them.

Formation of Sludges in Oil

H. Stäger (176) reported autoxidation combined with polymerization and condensation as the cause of decomposition of mineral oils. He showed (177) that two oils having identical tar numbers yielded upon heating in air under the same conditions 2.7 and 0.14% of sludge, respectively, with corresponding acid numbers of 0.92 and 0.10. This indicates that the tar number is not a safe criterion of the behavior of the oil in use. Stäger stated, too, that acid and sludge formation are not parallel processes.

Andrews (178) examined turbine oil deposits and found that the main cause of deposits in turbine oil is partial oxidation of the oil.

Rodman (179) investigated transformer oil sludge and described three types of sludges, the asphaltic, soap, and carbon sludges. He concluded that the asphaltic and soap sludges are produced most readily by poor oil, containing unsaturates, water, small resinous bodies, and
certain accelerators. The asphaltic sludge is an oxidation and polymerization product of attackable oil, and is the most general form of sludge. The soap sludge is a good carrier of moisture and oxygen. The carbon-type is produced during an electric breakdown.

Struninov\(^{(180)}\) experimented with methods of testing transformer oils and decided that air cannot be used in place of oxygen, nor can the precipitate be measured volumetrically instead of being weighed.

Stadničkov and Vozzinski\(^{(181)}\) found that sludges in insulating oils had their origin in the condensation of oxidation products formed by the oil.

Barnard, e\(_t\) al\(^{(182)}\), concluded that the primary cause of sludge formation is the oxidation product, asphaltene.

Experimental work by Marcusson and Bauerschäfer\(^{(183)}\) and von der Heyden and Typke\(^{(184)}\) has shown that a highly refined oil precipitates a greater amount of sludge than a less refined oil. The latter authors\(^{(185)}\) found that the presence of copper causes considerable increases in sludge formation in all test results.

Turbine oil deposits were examined by Salathe\(^{(186)}\) and Blakeley\(^{(187)}\). Salathe found 42.5% water, 13.6% aliphatic and naphthenic acids. He also showed the presence of acetaldehyde, esters, and soaps. Blakeley analyzed a turbine oil deposit, and showed that it consisted of moisture 0.5%, petroleum ether soluble oil 43.3%, oil soluble in ethyl ether but insoluble in petroleum ether 50.4%, asphaltic matter 2.2%, and insoluble matter 4.4%. The insoluble matter consisted chiefly of metallic iron.
Tanaka, Kubayuski, and Furihata\(^{(188)}\) have discussed autoxidation of hydrocarbon oils as a cause of sludge formation. A theoretical explanation is given, based on peroxide formation of an oxidizable substance, which explains why an added substance may act as an inhibitor or pro-oxidant.

Chernozhukov\(^{(189)}\) distinguishes three different kinds of sludge in turbine oil:

1. Sludge formed through the polymerization and oxidation of tarry substances and having the appearance of the so-called asphaltenes. This sludge is never formed in properly refined oils.

2. Sludge of a distinctly acid character formed through the oxidation and polymerization of unsaturated compounds, and the basic hydrocarbons of the oil. The sludge is usually a sticky and viscous mass of brownish color.

3. Sludge comprised of iron and copper salts from organic acids. They are formed through presence of water in the turbine, whereby ferrous hydroxide and other compounds of a similar nature are formed and which react with organic acids to form organic salts.
The corrosion of storage tanks and refinery equipment by petroleum products has taken a tremendous toll over the years. Dameron (190) estimated that the annual corrosion toll in West Texas will average 20% of the original cost of steel tankage. Oils from other sections of the country are not quite so severe from a corrosion standpoint, but more "sour" oils are being produced now than in previous years. Every effort is being made by the producers and refiners to find means of prolonging the life of equipment and tanks.

Corrosion of refinery equipment may be due to the action of sulfur compounds and dissolved salts and water which may be present in the oils during storage. Egloff (191) has discussed the causes of corrosion and has indicated the methods employed to reduce the corrosion for each step in the production and refining of oil.

**Corrosion Due to Sulfur**

Kalichevsky and Stagner (192) state that over a dozen sulfur compounds occurring in crude oil, as well as elemental sulfur itself, are corrosive or conducive to corrosiveness. Among these compounds are mercaptans, hydrogen sulfide, alkyl sulfates, sulfonic acids, and alkyl disulfides. Other compounds, such as carbon disulfide, sulfoxides, sulfones and thiophenes, are only slightly corrosive, if at all (193, 194). Heat and moisture increase the corrosiveness. Elemental sulfur, after the elimination of hydrogen sulfide, is usually considered the chief
cause of corrosiveness. Bignell (195) states that the greater part of the corrosion which occurs in and around tanks and refinery equipment can be traced to the effects of hydrogen sulfide associated with the petroleum. The hydrogen sulfide attacks the iron, forming iron sulfide in an extremely reactive form. On exposure to air this product is converted to iron oxide and free sulfur; this reaction is sometimes so vigorous that the reaction mass glows, and the contents of the tank may catch fire (73). The iron oxide formed is not very adherent and tends to scale off, reducing the effective thickness of the steel tank. The presence of water usually accelerates this action, as also does elevated temperatures.

Sulfur compounds tend to corrode copper, silver, bismut mercury, lead, zinc, tin as well as iron. Of these metals, copper, lead, zinc, tin and iron are used in refineries, iron being used to the greatest extent. Schmidt (196) is of the opinion that not all metals which resist acid corrosion are resistant to hydrogen sulfide. The use of an alloy composed of 56.6% Fe, 31.89% Ni, 4.34% Cr, and 6.93% Al, block tin, cyclops metal (Ni=18%, Cr=8%, Fe=bal.), and noncorrosive steels are recommended for refinery service. They are evidently for other service than tankage.

Corrosion Due to Dissolved Salts and Water

Water solution of sodium chloride, calcium chloride, and magnesium chloride are quite often associated with petroleum. On standing, these solutions separate from the oil and are drained from the storage
tanks. They are quite corrosive and attack the storage tanks rapidly. Dabrosktan (197) reports that oils containing these salts corrode refinery equipment due to the hydrogen chloride which is liberated during refining operations. The corrosion of oil-storage tanks by salt water used for ballast in oil tankers has been considered by Kistyakouskii (198) and Lewis (199). Runge (200) has investigated the corrosion of stills by salts dissolved in the oils. Fry, Duffek, and Kock (201) have investigated the corrosion of steel by gasoline containing varying amounts of sea water, and have found that the degree of attack depended not only on the amount of water present, but also on the physical state of the water as governed by temperature conditions. Precipitated or dispersed water readily attacked the steel if it was present to an extent greater than 15 parts per million by weight. Hand (202) claims that the corrosion of special steels is as rapid with sea water as in the case of plain steels. Mathews and Crosby (203) discuss the separation of salt water and silt from crude oil of the Healdton, Oklahoma field. Separation is very slow and as much as 0.2-0.4% water may be present even after six months' standing. These brines, which contaminate the oil, contain as much as 6.0% salt and some magnesium chloride. Considerable corrosion of equipment has resulted because of the presence of these brines. Oxygen and carbon dioxide dissolved in waters associated with petroleum and petroleum products are also responsible for corrosion difficulties (100, 202).
Corrosion of Steel by Oil

The corrosion of steel by sulfur compounds and dissolved salts has been discussed previously, to a limited extent. Many references do not indicate the exact corrosive material; however, the available information is given here.

Braun and Karelina (204) studied the resistance to corrosion of a high-phosphorus, copper-bearing steel, zinc-plated steel, lead-plated steel and tin-plated steel against benzene, kerosene, and water. The high-phosphorus, copper-bearing steel was found to be sufficiently resistant to benzene and kerosene and was recommended for use in fuel tanks for motor vehicles. Zinc-plated steel was found satisfactory for use in water tanks.

Gregoire (205) compared the corrosion effects of black fuel oil and gas oil on steel tanks over a long period of time. Contrary to expectation, corrosion was greater with the gas oil than with the fuel oil which contained sulfur and was contaminated with salt water. Reconditioning of the tanks used for gas-oil storage was necessary every three years, while the tanks used for storage of the black fuel oil required only occasional treatment. Grindin and Arubartsumyan (206) report that ordinary carbon steel containing 0.2% C is strongly attacked by cracked gasoline over a period of 500-700 days at room temperature. Coincident with the corrosion, autoxidation of the gasoline takes place. Stainless steels were not attacked by this gasoline after 400 days exposure. Wood, Shoely, and Trusty (194) investigated the action of elemental sulfur and other sulfur-containing compounds, normally found in
petroleum, dissolved in naphtha on various metals including iron. The general conclusions were that those solutions were not markedly corrosive to any of the metals tested except when water was present in appreciable quantities. The naphtha solutions of sulfur were most corrosive to copper, mercury, and silver. Corrosion increased with increase in temperature. Laduishnikova (207) investigated the corrosion of a Russian gasoline containing 0.45% S and a kerosene containing 1.684% S. She found that iron was attacked to a lesser degree than was lead or copper and brass. The kerosene was considerably the more corrosive. It was also observed that the corrosion was less severe if the samples were kept in the dark. This phenomenon is explained by the presence of unsaturated compounds in the gasoline which are oxidized in the presence of metals and light. The presence of moisture accelerated the corrosion.

Wagner (208) reports that tests were conducted by the Aluminum Company of America and the Parkersbury Rig and Reel Company to determine the relative corrosion of steel tanks and aluminum tanks. No further information pertaining to the results obtained was found.

Bospolov (209) maintains that cracked gasolines become corrosive only as a result of changes which take place under the influence of atmospheric oxygen and which may be catalyzed by the metal of the storage tank. In those tests, it was found that iron is not corroded to any great extent by dry gasoline. However, the rate and degree of corrosion was greatly increased if moisture was present.

The work of Mardor and Farnow (210) corroborates the work of Wood, Sheely and Trusty (194). Mardor and Farnow, using a lunar gaso-
line, found that iron was hardly attacked by fuel containing sulfur, ethyl mercaptan, carbon disulfide, or aliphatic sulfides. They did note, however, that there is a wide latitude in the extent of corrosion by the same fuel.

Bock and Kunzelman (211) find that light motor fuels and Diesel fuels readily attack iron as well as some other metals. Galvanizing or other treatment of the iron did not prevent corrosion from taking place. It is believed that the attack is due to the presence of sulfur compounds. Diesel oils obtained from coal tar are very corrosive.

Mollonio and Hottloton (212) inspected nine transformer tanks of the indoor type and of steel construction after twenty-seven years of service and found some evidences of corrosion. This was believed to be due to products formed by oxidation of the oil, although the presence of acid did not necessarily cause corrosion.

Steel tanks may be protected from corrosion to some extent in several different ways. Some of these, particularly the use of coatings, are discussed in the section on the storage of petroleum products. Others are discussed in the following paragraphs.

Nowcomb, Dixon, and Kelloy (213) recommend lining steel tanks with "Gunite", a reinforced concrete. They have found this to be a most practical means of preventing this corrosion. This article gives full details on the method of applying the "Gunite" which is applied by means of a cement gun. The cost of "Gunite" linings was found to be: $0.40 per square foot for roof and structural members, $0.375 per square foot for the shell, and $0.35 per square foot for the bottom of
the tanks. This cost was approximately one-half of the cost of a new steel tank of the same size. Other methods of protecting steel tanks from corrosion were also discussed. Their discussion was based on the experiences of several American Petroleum companies. The use of galvanized steel was found to be more satisfactory for both tanks and tank roofs than plain steel. Aluminum, either in form of foil or sheet, gave excellent service, but the main objection was its high initial cost. Neither lead foil nor any kind of paint was found satisfactory as a protection against corrosion. Cathodic protection was found very satisfactory in most instances for protecting the tank bottoms from corrosion.

Armico iron has been found satisfactory for containers for petroleum oils rich in sulfur compounds (214).

The use of sprayed aluminum coatings for the interiors of steel storage tanks has been proposed. While this type of coating provides a corrosion-resistant surface for both the oil and the vapors above the oil, still it is not always possible to obtain an uniform and continuous coating over the entire surface of the steel. The aluminum coating is rapidly removed from the lower parts of the tank where the separated water and brine solution collect, and, as a result, corrosion occurs at this location (215, 216).

The use of alkaline solutions is often employed to counteract the action of sulfur compounds and acidic substances present in the oil. Heidt has patented a process of treating the interior of tanks to prevent corrosion which consists of introducing ammonium hydroxide or am-
monia-liberating substance into the tank. The liberated ammonia is claimed to reduce and prevent corrosion(217).

Cathodic protection for the bottoms of storage tanks has been used to prevent corrosion (213, 218, 219). This method employs the use of a second metal electropositive with respect to the tank material, and which is placed a short distance above the tank bottom and held there by means of separators to prevent short circuiting and local contact. This method has proven successful in use.

Corrosion of Copper by Oil

Copper is corroded by the sulfur compounds in oil with the formation of a surface film of copper sulfide. It has been possible to set up a standard corrosion test for motor fuels and oils based on this phenomena. A description of this copper-strip corrosion test and other corrosion tests employing copper has been given by Garner and Evans(220). The corrosion effects of naphtha solutions of sulfur and sulfur compounds on various metals, including copper, has already been mentioned(194).

Another type of corrosion of copper is associated with the oxidation of the oil. Copper in contact with a cracked gasoline was corroded during a 600-day test at room temperature. The loss in weight of the copper was as much as 2.5%. In this particular work the corrosion was attributed to the autoxidation of the gasoline because samples of this gasoline which contained an oxidation inhibitor (α- or β-pinene) did not oxidize or corrode the copper(221). Arnstoine, Haringhouser and has found that the greatest amount of sludge was produced by copper
in contact with insulating oils when compared with tin and lead (222). Stäger (223) states that copper, along with lead and zinc, are attacked by the organic acids present in the oil.

**Corrosion of Lead by Oil**

Lead is corroded by the sulfur compounds in oil with the resultant formation of lead sulfide, and also by the organic acids present in the oil (211, 223). Bospolov (224) carried on a series of tests in which several metals and alloys were exposed to the action of petroleum distillates and vapors of these distillates. Lead was found to be particularly susceptible to corrosion by the hot vapors of cracked gasoline and was also severely attacked by lighter gasoline fractions.

Lead in bearings is often attacked by lubricants. Under some conditions, especially when the softer constituents are attacked, this corrosion of the bearings is beneficial and actually results in better lubrication. Under other conditions, the corrosion may be very destructive (225). Oxidized oils and oils containing free fatty acids or sulfur appeared to be the most corrosive. Raymond (226) reporting on the corrosion of copper-lead, hardened lead, cadmium-silver, and indium-plated bearings believes that bearing design is the cause of failure more often than the lubricant, and that corrosion effects were increased by relatively small rises in temperature. Jakeman and Hart (227) find that neither high-lead nor high-tin alloys is readily attacked by plain or compounded mineral oils.
In general, tin is corroded by petroleum oils in the same manner as copper and lead, but generally to a lesser degree (194, 211, 222, 224, 227).

Aluminum is resistant to the action of hydrogen sulfide and other sulfur compounds, and has been used for tanks and other vessels in petroleum refineries. Aluminum is readily corroded by brine solutions and dissolved salts. The use of dissolved chromates to inhibit the corrosion of aluminum has been patented by Field (228). George (229) has patented the use of alkaline, water-soluble, metal salts of beta-glucosides derived from succulent plants for the same purpose. Gindin and Armbartsumyan (230) investigated the corrosion of various metals and alloys by high-hydrocarbon fuels of Russian origin and found that magnesium was attacked more readily than aluminum. The presence of acids, peroxides, and tar formers, products of the autoxidation of the gasoline, was mainly responsible for the corrosion. The same conclusion was reached in the corrosion of zinc and zinc-plated steel by similar fuels (231). Under certain conditions a "passive film", believed to be a zinc salt of organic acids, is formed on the zinc surface and prevents further attack by the fuel. Bengough and Whitby (232) investigated the corrosion of a magnesium alloy (Elektron Alloy AM503) by a technical benzene mixture, a straight-run, paraffin-type aviation gasoline, and a naphthenic-type fuel. Their results indicated that the presence of moisture was necessary for corrosion to proceed.
The use of concrete reservoirs for the storage of petroleum and petroleum products did not have very wide application until the onset of World War I. The shortage of steel then, as again during World War II, caused the oil industry to turn to some other material of construction for oil-storage tanks. Many objections to the use of concrete have been raised, chief among them being that oil would be lost because of the porous structure of the concrete reservoir. In later years this objection has been overcome by the use of suitable tank linings.

Aroy (34), in reporting on the use of concrete reservoirs in the southwestern part of the United States, states that the oil penetrates into the concrete for a distance of 1-1/2 inches. Freeman (36) states that oil does not penetrate deeply into concrete reservoirs properly constructed. He recommends a surface treatment of sodium silicate to render the tanks impervious to oil. The resistance of concrete to reaction and penetration by oil may be prevented by the use of "Sika", a colloidal solution of light and heavy metals (54). The use of coatings composed of glue and glycerol, fixed by formaldehyde treatment has been claimed to prevent penetration of oil into concrete (58).

Schumann (233) states that oils, both mineral and vegetable oils, have a tendency to lower the physical strength of the concrete. The best remedy for this is to obtain as dense a concrete mixture as possible. Free fatty acids in oils have a disintegrating effect on the concrete due to reaction with the lime in the concrete to form lime soaps.
Smith (234) corroborates the effect of fatty acids mentioned by Schumann, but states that mineral oil has no injurious effect upon concrete. The tendency of oils to permeate the concrete is mentioned, and, for this reason, concrete tanks are not recommended for the storage of gasoline or kerosene. These tanks were satisfactory, however, for the storage of oils having a viscosity of 50 seconds Saybolt at 20°C. Waterhouse (235) agrees with Smith and Schumann that fatty acids cause considerable disintegration of the cement and recommends the use of water glass for water- and oil-proofing the storage tanks. Nazarov (236) reports on tests made to determine the action of kerosene on the tensile strength and impermeability of portland cement. Kerosene lowered the tensile strength of cement mainly because of penetration into the pores of the concrete. In three months time, the kerosene penetrated concrete to a distance of 0.2 to 0.3 cm.

Serkin (237) investigated the action of mineral, vegetable, and animal oils on concrete. He found that the structure of the concrete deteriorated due to the reaction of the fatty acids present in the animal and vegetable oils with the free lime present in the concrete. Mineral oils have no chemical effect on concrete unless acidic substances such as fatty acids, phenols, or other additives containing reactive substances are present. All three types of oils have a disintegrative action on concrete due to penetration of the oils into the concrete. Serkin recommends the use of admixtures in the concrete which will tend to produce a denser structure. These admixtures have the effect of accelerating the rate of solution of the cement compounds.
during the setting process. The use of impregnants such as solutions of silicates, fluosilicates, and resinous compositions is also recommended for the prevention or reduction of oil penetration into the concrete. The article of Frodl(238) is along the same vein as that of Serkin.

THE ACTION OF METALS AND OTHER SUBSTANCES ON PETROLEUM AND PETROLEUM PRODUCTS

The action of metals on oils is commonly associated with other phenomena such as the aging or deterioration of oils and the oxidation of oils. Since oils, for the most part, are stored and used in metallic equipment, it is important to know the results of metallic contact with the oil and what can be done to reduce the degree of aging, deterioration, or oxidation. Of the various metals and alloys, copper has probably received the most attention and lead, iron, and the other metals considerably less.

Action of Copper on Oil

Electrical transformers, switches, and circuit breakers employ considerable amounts of copper in their construction. It is desirable to maintain the oils used for insulating purposes in good shape over a long period of time. The contact of the oil with the copper wiring tends, in time, to accelerate the oxidation resulting in an increase of the acidity of the oil and the formation of sludge(239).
Evidently, some of the copper is dissolved in the oil, and this dissolved copper is believed to be the catalyst. Chernozhukov, Kurlin and Kurlina (240) are of the belief that copper is most active in catalyzing the formation of acids, which are later converted to hydroxyacids. Eventually, solid deposits form and separate from the oil.

Yamada (241) investigated the relative catalytic influence of a number of metals on the formation of sludge and acid in transformer oils by heating the oil at 140°C for a period of 100 hours in contact with air and the metal. The action of the metals varies with the degree of refining of the oil. With highly refined oils, which may contain sulfonic acids or metallic salts of sulfonic acids, certain metals tend to reduce the acidity and form metallic salts. With less highly refined oils, certain metals and alloys, copper and brass particularly, increase the amount of sludge formed considerably. It was also found that those metals which tended to accelerate sludge formation generally increased the acidity of the oil.

Von der Heyden and Typke (242) in a test similar to that of Yamada (241) find that copper, alone or in combination with other metals, had an unfavorable effect upon the oil, resulting in acid formation and the production of deposits. These investigators conducted their tests in both the presence and absence of oxygen and by heating the oil in the presence of metals to 120°C for 70 hours.

Stäger (223) reports that copper and brass had a catalytic effect on the deterioration of transformer oils and that these substances favored the formation of deposits in the oil. The amount of
deposit depended on the amount of metal exposed. The copper was attacked by the organic acids present in the oil, resulting in the formation of compounds of high molecular weight.

Tychinin and Butkov(243) investigated the composition of the sludges formed in transformer oils, and found that those sludges consisted of the salts of organic acids having 11 to 22 carbon atoms produced by the oxidation of the oils. The oxidation was accelerated greatly by the presence of copper.

Chernozhukov, Kurlin, and Kurlina(240), in the investigation referred to above, found that copper catalyzed the oxidation of naphthenes to asphaltic substances. Larson and Armfield(244) investigated the catalytic effect of metals on the oxidation of lubricating oils prepared from Pennsylvania, Mid-Continent, and California Petroloums and found copper readily catalyzed the oxidation of all three types of oils.

Cupit(245) found that copper had the greatest catalytic effect on the oxidation of mineral oils. Other metals employed as oxidation catalysts included metallic iron, tin, aluminum, and nickel. Oxide catalysts, such as vanadium pentoxide, cuprous oxide, and cupric oxide, were also investigated. Cupit found that both uncracked and cracked distillates were readily oxidized.

The deleterious effect of copper on several types of petroleum oils has been confirmed by many investigators(246, 247, 248, 249, 250, 251, 252).
Effect of Iron on Petroleum Oils

Iron, as cast iron, cast steel, and worked steel, is used to a greater extent than any other single material in the construction of all types of equipment. It is used for oil storage tanks, refinery equipment, gasoline and Diesel motors, transformer cores and shells, switches, and circuit breakers. The temperatures existing in such equipment vary considerably and because of this the action of the iron on the oil is variable.

Chernozhukov, Kurlin, and Kurlina\(^{(240)}\) found that iron, only to a smaller degree than copper, catalyzed the rate of formation of acidity and solid deposits in mineral oil used for transformer insulation. They found that iron had a tendency to catalyze the oxidation of the constituents of the mineral oil to phenols.

Yamada\(^{(241)}\) claims that iron tends to reduce the acidity of highly refined transformer oils due to the formation of an iron salt of sulfonic acids originally present in the oil.

Stäger\(^{(223)}\) claims that iron has no effect on the formation of deposits in transformer oil. This view is also shared by other investigators\(^{(243, 245)}\). Other investigators, however, take the opposite view\(^{(244, 247, 248, 250, 251, 253)}\). That iron does have some action on petroleum oils, has been definitely proven by Chernozhukov\(^{(255)}\), Stadnikov and Vozinskaya\(^{(256)}\), and Boisselot and Mouratoff\(^{(257)}\), who investigated the sludge separated from transformer oils and found iron to be present. American investigators\(^{(244, 247, 250, 251)}\) are of the
opinion that finely divided iron, such as iron filings or powdered iron, and iron present in the oil as naphthenates definitely cause the deterioration of motor oils. The determination of the amounts of iron in the oil and sludges withdrawn from automobile motors after test is considered of great importance.

**Effect of Lead, Tin, and Other Metals on Oil**

Haringheuzen and Was (239) find that the effect of lead on transformer oils is less than that of copper. Yamada (241) states that lead tends to reduce the acidity of highly refined oils due to the formation of salts of acids present originally in the oil, but with less highly refined oils, lead is very active in accelerating the formation of sludge. Stäger (223) has found that the organic acids produced during the oxidation of transformer oils readily attack lead, and that this oxidation is catalyzed by the presence of lead. Acids of low-molecular weight, formed in this lead-catalyzed oxidation, are peculiar in that they are insoluble in the oil. The acids formed during oxidation of oils are usually soluble in the oil.

Tyohinin and Butkov (243) state that lead is more active than copper in the oxidation of transformer oils. Larsen and Armfield (244) found that while copper was the most active catalyst at low ratios of surface to oil volume in the oxidation of lubricating oil prepared from Pennsylvania, Mid-Continent, and California crudes, lead surpassed copper at higher ratios. The action of iron was similar to that of lead.

The use of lead tetraethyl as an antioxidant has been reported by Hatta (258). Oxidation was definitely decreased in turbine oils prepared from
paraffin-base crudes, which contained small amounts of lead tetraethyl. However, the opposite was the case when naphthenic-type oils were employed. The acid and saponification values, specific gravity, and sludge formation were all distinctly increased by the presence of lead tetraethyl.

Tin does not appear to have near the catalytic effect as copper, lead, or iron on the oxidation of mineral oils and may even be considered as an antioxidant in some cases (239, 241, 243, 245, 249).

Aluminum, zinc, magnesium, and nickel have a very minor effect as catalysts on the oxidation of the oil (241, 242, 223, 245, 249). However, if they are present in a combined form, such as oleates or stearates, their activity is increased (254).

Action of Other Substances on Oil

Yamada (259) states that the presence of unsaturated compounds and sulfur together in a transformer oil will result in sludging of the oil. Proper refining to produce a white transformer oil usually corrects the trouble.

The presence of such organic acids as stearic, oleic, benzoic, and naphthenic acids accelerates the oxidation of highly refined mineral oils (260). Small amounts of metallic soaps also accelerate oil oxidation (254, 260). Of these metallic soaps, the oleates of aluminum, copper, and iron had the greatest effect, while those of tin and chromium had a small effect compared to that of copper and iron. In some cases, tin oleate had an inhibitory effect on the oxidation of oils.
Minkin\(^{(262)}\) reports that oil paint taken from the walls of an oil tank used in a turbine-oil circulating system had a strong catalytic effect on the oxidation of the oil. He recommends that the surface of the tank be covered with an anticorrosion coating instead of paint to overcome this action. Bruckman and Halobos\(^{(254)}\) report that lead compounds, such as those which occur in paint, are responsible for oxidation of oils.

According to Aleksandriiskaya and Koritskii\(^{(263)}\) glyptal varnishes prepared with glyptal resin in linseed and linseed oils cause oxidation of transformer oils, resulting in a considerable increase in the acid number.

Vorob'ev and Prikhod'ko\(^{(264)}\) investigated the effect of coumarone resin on the properties of transformer oils. They found that transformer oils containing coumarone resin did not change their surface tension after exposure to oxygen or humid air. The acidity was reduced and the stability was not impaired. The addition of 0.2-0.5% coumarone appears to be the optimum, but varies with each oil.

**Analytical Methods**

Since it is apparent that metals are active in the oxidation and deterioration of oil, it is essential to maintain a control on the oils so that this deterioration can be kept to a minimum. Assaf and Hollebaugh\(^{(265)}\) and Lykken, Fitzsimons, Fibetts, and Wyld\(^{(266)}\) have written articles dealing with the analytical determination of various metals in new or used petroleum oils. These articles should be consulted for details.
EFFECT OF VARIOUS FACTORS ON THE STABILITY OF OIL

In service, oil is subjected not only to the action of metals and the atmosphere at the temperatures of operation, but also to the action of light and radiation, moisture either as steam or condensed water, high and low temperatures, and may other factors which cause the oil to deteriorate. The literature on the effect of some of these factors has already been discussed in other sections of this report. The remainder will be discussed here.

Effect of Residual Acidity on Petroleum Oils

Highly refined oils often contain residual sulfonic acids or salts of sulfonic acids dissolved in the oil. On contact with metals, the acidity is reduced with the formation of metallic salts of the sulfonic acids (241). The darkening of transformer oils on heating has been attributed to the presence of sulfur compounds, such as dissolved sulfonic acids (259). Pyhala (267) asserts that the failure of turbine oils is due to the presence of sulfur compounds produced during the sulfuric acid treatment of the oil.

Effect of Moisture on Petroleum Oils

The presence of water in an insulating oil reduces its insulating properties and the presence of as little as 0.08% water destroys them completely (268). Becker (269) states that the amount of water should be less than 0.033%. The underlying theory of the breakdown
mechanism of moist insulating oil has been discussed by Gyomant (270). He believes that small water drops, emulsified in oil tend to assume an ellipsoidal form. In the presence of a strong electrical field these drops are oriented in such a way that channels are formed throughout the oil and short-circuiting occurs along these channels. Hirai (280) has found that at constant temperature the breakdown voltage decreases as the water content increases, and that at constant water content the breakdown voltage increases as the temperature increases.

The solubility of water in mineral oils has been discussed by Flourrs and Dietrich (281).

The emulsification of oil with water will destroy the lubricating properties of oils and for this reason every effort is made to keep emulsion formation to a minimum in turbine oil systems. The emulsifying tendency of an oil increases with the presence of alkali or soap (288). The presence of finely divided oxidized material tends to stabilize emulsions. This has been rated in the operation of light oil recovery plants (282). Solomon (283) in discussing the deterioration of steam-turbine oils in service discusses the factors which tend to increase the tendency of the oil to emulsify with water. He couples the formation of insoluble matter by oxidation and the subsequent increase in viscosity with this tendency.

Matthews (284) asserts that oxidation of lubricating oils is caused by the presence of moisture which contains oxygen. The moisture is drawn into the engine crankcase or oil tanks through the breather pipe and is absorbed by the oil as it cools.
Effect of Light on Petroleum Oils

It has been observed by many investigators that petroleum distillates exposed to the action of sunlight or other radiation gradually changed the appearance of the oil and resulted in the formation of insoluble products. Waters (285) exposed samples of lubricating oils to the action of the air and sunlight. Over a period of 132 days it was noted that the oil gained from 27 to 37% in weight while giving off carbon dioxide and water in the oxidation process. In a shorter test of 23 days' duration between 1-3% of material insoluble in petroleum ether was formed. The acidity of the oil, calculated as oleic acid, increased from below 0.1% to above 3%. The precipitate insoluble in petroleum ether contained 19.45% of oxygen, although the original oil contained no oxygen. Oxygen-containing substances, soluble in the oil, were also present in the oil after the oxidation.

Kharichkov (286) found that oxidation of petroleum oils in air and under the action of sunlight and also diffused light, produced monobasic naphthenic acids which would combine into complex polybasic acids. These acids are similar to those obtained in the alkali treatment of oils.

Vellinger and Marchand (287) studied the effect of light on mineral oils dissolved in various solvents and found that the oils change on exposure to the light according to the nature of the solvent. Of the solvents employed, the observed changes were greatest in carbon tetrachloride, chloroform, and amyl alcohol; no change was observed with acetone or ethyl ether. The oils discolor in the absence of air, and
this change is ascribed to the formation of soluble polymerization products. When the samples are exposed to the air simultaneously with light, the color change is not so distinctive, but insoluble oxidation products are formed.

Inozi (288) exposed samples of American, Russian, and Galician transformer oils to light for a period of three years. Considerable changes in the oils occurred in the oils after three months' exposure as measured by changes in sludge value, tar number, and acid number. It appears that oxygen is necessary for this change because samples of the various oils stored in the dark in completely filled containers showed no change whatsoever. Heydon and Typko (289) observed the same phenomena in tests extending over one and one-half years. On extending these tests to three years, similar results were obtained. It was noted that increases in the acid numbers increased as the time of exposure increased (290).

Vellinger (291) exposed mineral oils to the action of oxygen at room temperature to the light of a tungsten-filament electric-light bulb and observed that the oils darkened in color with the time of exposure. The oils are oxidized, and the oxidation progresses even to the formation of carbon monoxide, carbon dioxide, and water. Of the various oils tested in this manner, those from Venezuela, Texas, Pennsylvania, and Colombia show little difference in their photo-oxidation characteristics; thoroughly refined Russian oils show evidence of autocatalytic oxidation. The interfacial-tension of the oils with water is greatly affected by photooxidation, Venezuelan oils being affected to the greatest extent.
The effect of radiation from a mercury vapor lamp on the oxidation of motor fuels has been investigated by Vellinger and Radulesco (292, 293). They found that the absorption of oxygen is a function of the time of irradiation. The main product of this photo-oxidation was gummy material which varied according to the pre-treatment of the sample.

Rysselberge (294, 295) has employed ultraviolet light of 3000-4000 A. to determine the condition of insulating and lubricating oils during service. The fluorescence of the oils changes as oxidation progresses, and the color of the fluorescence gradually changes from a blue or violet to green.

**Effect of Temperature on Petroleum Oils**

The behavior of oils varies considerably with the temperatures employed and the atmosphere. Much information is available on the thermal and catalytic cracking of oils at elevated pressures and temperatures, but this information is believed to be outside of the scope of this report. Also, much information concerning the formation of deposits in internal combustion engines is available, but the temperatures are considerably above the temperatures to which oils may be subjected during storage.

The deterioration of oils at elevated temperatures and in the presence of oxygen increases as the temperature increases (see section on Oxidation of Petroleum Oils). The oxidation proceeds very slowly at low temperatures (below 100°C.), and the life of the oil is considerably greater when maintained below 100°C. The long life of transformer oils in service is due to low temperatures and the use of inert atmospheres.
over the oils. In general, it can be said that excessive deterioration of petroleum oils will not occur at temperatures up to 170°F. Gasolines and other light distillates will suffer due to evaporation of the more volatile constituents and decrease in octane rating. Various methods for the reduction of evaporation losses have been discussed in a previous section. Viscosity changes occur and the oil tends to thin out as the temperature changes, but it is believed that no great change will occur in the range of 60° - 160°F.

As temperatures are lowered, oils tend to become viscous and gel. This is due to the crystallization of paraffin wax in a very finely divided form (296). As the temperature is lowered, the resistance to flow is increased until a point is reached where the oil will not flow. Various proprietary preparations have been developed to improve the flow characteristics of oil at low temperatures, and these are described in the section on additives for petroleum oils. Woog, Ganster, and Conlon (297) report that asphaltic and naphthenic oils rapidly cooled to a low temperature tend to form "glasses", but slow and prolonged cooling permits crystal growth. Woog, Girandan, and Doyan (298) discuss the alternate heating and cooling of oils, and find that oil heated to 100° for 15 minutes, then maintained at 0°C, for one hour, and finally chilled to -75°C, and allowed to warm up will have a lower pour point than the original oil before such treatment. Changes of as much as 25.8°C. have been observed.

In the storage of oils within a temperature range of -60°F. to +170°F., very little can be said of the behavior of oils, other than
a. Oils tend to become viscous and solidify at low temperature.
b. The viscosity change between 60°F. and 160°F. will not be
great in properly prepared oils.
c. Motor fuels and light distillates will tend to shrink in
volume, because of evaporation losses.
d. Oxidation reactions will be slow and can be retarded by
maintaining an inert atmosphere above the oil.

In procuring oils for a long-term storage program, considerable
testing will be required to find desirable oils. Manufacturer’s recom-
mandations will be of value.

**ADDITION AGENTS**

The quality of petroleum oils may be improved, not only by re-
fining to remove objectionable components of the oil, but also by the
addition of certain chemicals which compensate for the inherent un-
derirable characteristics of an oil. The additive agents consist of
oxidation inhibitors, corrosion inhibitors, chemical inhibitors of gum
formation, pour point depressors, oiliness carriers, viscosity index
improvers, and fluorescence improvers. Before the discovery of oxidation
inhibitors, it was supposed that oil stability depended on inherent re-
sistance of oil molecules to oxidation, and exhaustive oil refining to
remove unstable constituents was believed to produce the most stable oil.
The effect of the oxidation inhibitors which protects less stable mole-
cules is attributed to the prolonging of the period of induction of the
oxidation reaction. The action of corrosion inhibitors is believed to
be caused by the passivating of metal surfaces which otherwise would catalyze the oxidation reaction (299).

In this section oxidation inhibitors, corrosive inhibitors, additives and inhibitors to prevent formation of deposits, and pour point depressants will be discussed.

**Oxidation Inhibitors**

Byers (300) summarized American patents on antioxidation agents for lubricating oils from 1917 to 1936. Van Voorhis (301) gave a complete summary of all lubricant additive patents issued during 1938 and 1939. The patent literature on oiliness agents was reported by Byers (302).

A review of oxidation inhibitors in insulating oils was given by Berberich (303), who emphasized the need for a standard test to evaluate inhibitor effectiveness. Schmurmann (304) discussed the use of oxidation inhibitors, besides other classes of additives.

**Oxidation Inhibitors in Turbine Oils**

The unusual instance of the failure of a turbine oil after nine years was reported by Williams (305). By peroxide determinations and chromatographic separation of the oxidized products, the course of the deterioration was shown to be similar to that of the atmospheric oxidation of fatty oils with an induction period followed by a period of rapid oxidation.

C. Candea and C. Manughevic (306) heated a Rumanian turbine oil to 100, 200, and 300° to determine the inhibiting effects of various oxidation inhibitors. The oil was oxidized in the absence and presence
of 0.02 - 1% of the following inhibitors: thymol, toluidine, anthracene, naphthalene, paraffin, and tetra-methyl-p-diamino-diphenylmethane, all of which showed some effects toward retarding the oxidation of the oil. The authors concluded that for any given temperature there is a limit to the amount of added inhibitor beyond which the inhibiting effect is no longer apparent. Herlocker and co-workers (307) obtained a U. S. patent on an oxidation inhibitor which consisted of morpholino-methyl-B-naphthol in small amounts, such as .05 to 1.0%. The use of inhibitors in turbine oil was reviewed by Petersen (308) and Baker (309).

Oxidation Inhibitors in Transformer Oils

The effect of inhibitors on transformer oils was discussed by Clifford (310), Vellinger and Saito (311), Typke (312), and Butkov (313). All of the compounds used by these workers fell into two classes. The one class was aromatic amines, such as aniline, o-toluidine, and naphthylamine, and the other phenols, such as B-naphthol. Vellinger and Saito showed that copper and copper stearate diminish the activity of antioxidant, the latter being the most troublesome. Butkov showed that if 1% B-naphthol were added to a transformer oil before testing for two hours at 150° with oxygen at 15 atmospheres pressure, the action of oxygen was decreased as shown by the following data, with and without oxidant: acid number 0.35, 16.76; saponification number 2.06, 38.26; sulfuric acid-soluble 3.0 and 23.0%. Mizushema (314) showed that the oxidation of white oil was inhibited by the addition of 2 - 8% of crude transformer oil. He attributed the protective action of the crude oil to its sulfur content. Copper caused a considerable decrease in the
antioxidizing action of crude oil, and this was believed to be due to the removal of sulfur by the sludge, which was increased by the action of copper with the formation of copper sulfide.

Oxidation Inhibitors in Mineral Oils

The use of antioxidants in mineral oils was reported in Rubber Age\(^{(315)}\) by Marcusson and Bauerschifer\(^{(316)}\) and by Vellinger and Radulesco\(^{(317)}\). Aldol-a-naphthylamine (agents), which has already proved itself of great value in retarding the oxidation of vulcanized rubber, similarly, stabilizes the oils. Vellinger and Radulesco showed that crude oil has greater resistance to oxidation than refined oil.

Krein\(^{(318,319,320)}\) reported in a series of articles on increasing the stability of mineral oils by means of inhibitors of oxidation. He studied the effects of 19 various antioxidants. He concluded that in normally refined oils the formation of oxidation products is reduced by 30 - 50\%, depending on the chemical composition of the oils. He showed, too, that the effect of antioxidants is selective. The amine- and phenol-type compounds decrease the formation of acids, but increase the amount of condensation product. Lead tetraethyl, tin tetraethyl, and tin oleate retard the processes of oxidation and polymerization. Mixtures of antioxidants do not decrease the formation of residues. Krein stated that well-refined oils are stabilized easily, and that the most active antioxidants have no unfavorable effect on the properties of the oil. In a study of the effect of inhibitors on pure hydrocarbons, Krein showed that inhibitors protect paraffins the most, then naphthenes and isoparaffins. Most difficult to stabilize are naphthene-aromatic hydrocarbons of the tetralin type.
Assaf and Balsbaugh(321) investigated the effect of thioethers, disulfides, and mercaptans as additives, because these compounds are normally found in commercial refined oil. They reported the effects of six other oxidation inhibitors in oil in the presence and absence of copper. These authors stated that the nonhydrocarbon constituents of a mineral oil determine to a large extent the characteristics of an oil under limited oxidation.

Lewis and co-workers(322, 323) examined redwood products as inhibitors of oxidation of petroleum hydrocarbons. They showed that the ethyl acetate-soluble part of the tannin fraction was an effective inhibitor of oxidation of mineral oil, but of little value in protecting gasoline.

The autoxidation of lubricating oil is discussed by Fukagawa and Cho(324). It was shown that oxidation of lubricating oil is increased by calcium chloride, alcohols, and aldehydes. Sulphur and alpha and beta naphthol were found to have excellent antioxidizing properties. A review article on the use of inhibitors to retard the oxidation of lubricating oils was published by E. Villar(325). Inhibitives were classed by him as hydrocarbons, phenols, ethers, and amino ethers, chlorine, nitrogen, sulfur, and phosphorus compounds, organometallic compounds, and sulfonic acids.

The blending of oils in order to increase their resistance to oxidation was investigated by Thurn(326) and Thiessen and Gratzi(327). Control of fuel oil sludge was studied by Mitchell(328). The stability of germ process oils was discussed by Southcombe(329) and Lowry(330).
Oxidation Inhibitors in Gasoline

Mouren and Dufraisse\(^{331}\) were the first to demonstrate the existence of oxidation inhibitors. Before their discovery, oil stability had been associated with inherent resistance of molecules toward oxidation, and oil refining was thought to remove all unstable compounds present. Since then these authors\(^{332}\) have extensively investigated the autoxidation and antioxygen effect in fuels. Mondain-Monval\(^{333}\) has investigated the formation of peroxides in the oxidation of hydrocarbons.

A review article on effect of antioxidants in motor fuels is followed by an account of experiments on samples of Rumanian gasoline inhibited by .01% of various phenols and aromatic amines by Candea and Cristodulo\(^{334}\). They reported that the tendency toward oxidation paralleled gum formation, but antioxidants had little effect on the oxidation to form aldehydes and acids.

Scheumann and Haslam\(^{335}\) have examined pyrogallol derivatives as gasoline antioxidants, but point out that these compounds have the disadvantage of being soluble in whatever water that may separate from the gasoline. Rogers and Voorhees\(^{336}\) reported that monosubstituted aminophenols are good antioxidants or inhibitors of gasoline.

Dryer and co-workers\(^{337}\) and Degtyuieva\(^{338}\) have investigated use of antioxidants in the stabilization of cracked gasolines. Degtyuieva found the best stabilizer to be hydroquinone followed by pyrogallol. Sukhankin\(^{339}\) reported that stabilization of crude oil provides the highest yield of gasoline. Some autoxidation reactions of gasoline are discussed by Graetz\(^{340}\).
Corrosion Inhibitors and Rust Preventives

The ordinary oxidation inhibitor functions because it prolongs the period of induction of the oxidation reaction. A second type of inhibitor, the so-called corrosion inhibitors, is believed to act by passivity of the catalytic activity of metals. These inhibitors are made up of organometallic compounds of phosphorus, arsenic, and antimony (341). The organic compound of chromium, bismuth, mercury seem to behave similarly.

The Santaloubes (342) are commercial corrosion inhibitors of organic phosphite or a nonester type of organic compound of phosphorus. Most of the available information about this subject is in the patent literature.

A review of data on slushing-type rust preventives is given by Bishkin (343). A discussion of rust preventives has been reported by Tarson (344), Barnes and Deegan (345), Houghson and Company (346), Thinson and Clark (347), and Albin (348).

Jakeman (349) has carried out experiments with Lanolin Rust Preventives. Britton (350) has reported on protection from rust in the petroleum industry. Genta (351) described experiments in detail on the corrosion of interior of oil flow tanks. Kjerman and Bergstedt (352) investigated the efficiencies of 22 different antirust agents. The effectiveness of oils for rust protection was reported by Heinrich and South (353).

Calloman (354) has outlined theories of corrosion with a discussion of the physical and chemical properties of alloys with particular
merit for meeting the corrosion problems of the oil industry. Perak and Wenzel\(^{(355)}\) gave a detailed classification and listing of a large number of inhibitors with numerous references and a list of patents.

### Additives

Hamilton and Keyser\(^{(356)}\) published an all-inclusive review of the development of addition agents for fuels and lubricants. Fuel additives and lubricant additives are classified by their functions, and the types of material in commercial use are described briefly. The patent literature on the subject is reviewed, particularly the technical literature on lubricant additives. Byers\(^{(357)}\) has discussed the trend in extreme-pressure lubricating oil, as shown by patents.

Rieff\(^{(358)}\) has shown that phenolic compounds and their metal derivatives are advantageous lubricating oil addition agents. The use of phosphorus sulfide organic reaction products as lubricating oil additives was investigated by Pritzker\(^{(359)}\). Lubricating oil addition agents have been investigated by Thomas\(^{(360)}\), Myers\(^{(361)}\), Prutton\(^{(362)}\), Musgrave\(^{(363)}\), and Foster\(^{(364)}\).

The influence of addition of vegetable oils was examined by Balada\(^{(365)}\). Jacobs and Othmer\(^{(366)}\) have shown that commercial soybean lecithin is an effective lubricating oil inhibitor.

Additive agents for special-purpose oils have been reported. Miller and co-workers\(^{(367)}\) discussed the use of additives in automotive lubricants. Sloane and Maverich\(^{(368)}\) have reported on additive agents for motor fuels. Pritchard\(^{(369)}\) discussed the use of additives in the steel plant. Thiemann\(^{(370)}\) and Heinze\(^{(371)}\) have investigated the usefulness of additives in Diesel fuels.
Chemical Inhibitors of Gum Formation

The action of aging inhibitors upon mineral lubricants was investigated by Schildwachter and Unverhan. Results are presented of the effect of oil inhibitors on sludging and corrosion in engine tests. Byers has discussed the patent literature on additives on synthetic lubricants. The action of aging inhibitors on lubricating oil was discussed by Snider and Franchetti. The mechanism of sulfur inhibition on lubricating oils was examined by Denisin and Condit.

The action of chemical inhibitors of gum formation in gasoline has been investigated exhaustively by Egloff and co-workers. Ross and Henderson have shown that polymer gas can be readily stabilized against gum formation by commercial inhibitors. Inhibitory action of various substances on the deterioration of cracked gasoline has been investigated by Mardes and Vol'f and Vasileva. Rees and co-workers have investigated the use of lecithin obtained from soybeans as a gum inhibitor in gasoline. Vol'f and Vasileva have made experiments on the influence of high storage temperatures, and of iron on the stabilizing influence of gasoline inhibitors. Byers has reported on the abstracts of patents of gum inhibitors.

Pour Point Depressants

A thorough discussion of pour point depressants is given by Kalichevsky. Byers made a survey of the patent literature on pour point inhibitors. Hodges and Boehm have investigated
pour-point stability of treated oils under winter storage conditions. Aleksandriiskaya\(^{(391)}\) has investigated the lowering of the solidification point of transformer oils.

**SERVICE LIFE OF OILS AND RECONDITIONING OF OILS**

Not too much information is available on the service of oils over a long period of years. The best information available concerns the service of turbine and transformer oils which operate within relatively narrow temperature ranges. Peterson\(^{(308)}\) surveyed the service data on inhibited turbine oils which had been used in 560 steam turbines. He found that these oils showed a retention of essential properties after 14 years of service. Bruckman and Haalebos\(^{(254)}\) reported on transformer oils that had been in service for 30 years. They found that the materials which tended to deteriorate the oil included lead compounds (i.e., paint), iron, pine wood, and aluminum, the latter probably in the form of oleates used as a treating agent for the cloth insulation. Mellonie and Nettleton\(^{(212)}\) report on the condition of transformers and transformer oils after 27 years' service. They were concerned with acid and sludge formation in the oils. This article contains several suggestions for keeping the oil in good condition and they emphasize the need of keeping oxygen and moisture from the oil.

Texier\(^{(406)}\) recommends that transformer oils be maintained in condition by filtering under vacuum to remove moisture and solid particles. A disc-type filter is used in this conditioning treatment. Other investigators have also recommended purification by filtration\(^{(407, 408, 409)}\).
The water and solid impurities may be removed from transformer, turbine, and machine oils by means of a centrifuge, and several investigators have discussed the purification of oil by this means (410, 411, 412, 413).

Used oils may be reclaimed by treatment with adsorptive materials, followed by settling and filtration or centrifuging. Graefe (414) describes thirteen different processes for reclaiming oil. Most of these processes comprise treatment with fuller's earth followed by filtration and removal of water and light fraction, such as gasoline, by heating with agitation and under a vacuum. The cost of reclaiming oils in this manner ranges from $0.03 to $0.13 per gallon.

Housley (415) describes a purification process for transformer oil in which the oil is first centrifuged or dried in a blotter press to remove sludge and water, and then contacted with activated alumina to remove organic acids in solution in the oil. Activated alumina of 4-8-mesh size is used, and it may be reactivated. The use of activated alumina for reducing the acidity of transformer oils has also been discussed by other writers (416, 417, 418).

The use of adsorptive clays for regeneration of transformer oils has been discussed by Wischin (419), Soya (420), and Kvartin (421). Kimpflin (422) claims that the life of transformer oils can be prolonged 5 to 8 years by treatment with adsorptive earths.

Many writers believe that a more drastic treatment is necessary to restore the oil to its original condition. Typke (423) believes that treatment with adsorptive earths alone is not sufficient for most oils,
and a treatment with sulfuric acid or with sulfuric acid and sodium hydroxide solution is required. This may be followed by treatment with adsorbent earths for improvement of color of the oils. Most writers prefer a combination of treatments with acid, alkali, and absorbent earths (424, 425, 426, 427).

Berthelot (42c) suggests a pretreatment with a sodium salt such as the silicate, phosphate, aluminate, or tungstate which coagulates the finely divided particles. This sludge and the water are removed by centrifuging. Dietrich (429) employs less than 0.1% of triethanolamine for coagulating the impurities, and follows this pretreatment with centrifuging.
SYNTHETIC OILS

Experimental work on synthetic oils has been concerned largely with the preparation of synthetic lubricating oils. The synthesis of hydro-carbon oils has been carried out by the polymerization of polymer gas and olefins or by the gasification and hydrogenation of coal. Another group of synthetic oils that has received attention lately is the organo-silicon compounds.

Byers has reported on the patent literature of synthetic lubricants. Weil(393) has reviewed and surveyed research and developments in synthetic lubricants. Weil stated that owing to the high cost of synthesis and domestic abundance of lubricating-oil stocks, it is generally believed that synthetic lubricants will not be prepared in quantity in the immediate future. Evans(394) has classified compounds which have been patented as chemical addition agents for petroleum products, particularly lubricating oils.

Koch(395) and Barnard(396) have reported on production of synthetic oils by the polymerization of olefins by aluminum chloride. Barnard stated that these oils are resistant to sludge formation. Koch considered these equal to, or better than, the natural product.

Aldrich(397) described the preparation of a synthetic lubricant by the Kuhlman-Lestaquo process using as raw materials, Fischor-Tropsch gas-oil, benzene and dichloro-ethano. The upper-layer oil is reported to be of extremely good quality. Two papers were published(398, 399), which discussed the preparation of lubricating oils by the Bergins process for the treatment of coal. Mayor(400), reported on wartime substi-
tutes for petroleum oils in occupied France.

The use of silicones as synthetic lubricants has been reported by Kratzer and co-workers(401), Bass and co-workers(402), Kauppi and Pederson(403) and General Electric Company(404). Bass, et al, described the replacement of chlorine atoms in silicon tetrachloride by hydrocarbon chains by the Grignard reaction, followed by hydrolysis to hydroxyorgano-silanes and condensation to siloxanes. The polymers are reported to have the valuable properties of inertness to metals, high-temperature lubricants, and resistance to chemicals. Kauppi and Pederson(403) compared the characteristics and physical properties of silicone greases with petroleum fluids. Because of their high-oxidation resistance and low volatility, the silicones are finding useful application under severe operating conditions. The General Electric Company(404) has reported that the viscosity of silicone oils is remarkably constant over varying operating conditions. The General Electric silicone oils have a much higher degree of resistance to chemical change than petroleum oils. Since they are so highly immune to the deleterious effects of high temperature, as well as variations in temperature, they retain their original chemical structure under conditions of heat which would cause reaction in petroleum oils. Silicone oils are remarkably stable toward heat and oxidation and inert towards metals and many plastics. Copper, brass, bronze, aluminum, magnesium, steel, tin, cadmium, and chromium are not affected by it, even after heating at 300°F for weeks in the presence of air. Silicone oils are miscible with petroleum ether, naphthas, ether, benzene, toluene, xylene, chloroform, carbon tetrachloride, amyl alcohol, and ethyl
acetate. They are only partially miscible with methanol, ethanol, propylene, butanol, and acetone. They are immiscible with water and petroleum oils. Silicone hydraulic oil will change in viscosity less than 5% during storage for a year in glass or tinned containers. No sludge or precipitates form during this time. The oils remain fluid during prolonged storage at low temperatures, over 600 hours at -70°C, (-94°F).

GREASES

Greases are essentially gels produced by the blending together of a soap and lubricating oil on heating. While hot, they are quite fluid, but on cooling they solidify to a paste-like gel. Many types of greases are manufactured and used in industry. Of the different types of greases, the calcium, sodium, aluminum, and lithium-base greases are probably the most important.

Greases are used for two main purposes: (1) lubrication, and (2) preservation of equipment. The properties desirable in those two types of grease are considerably different: those used for the preservation of equipment must be extremely stable over a long period of time and must not have a corrosive action on the article. Those used for lubricating purposes must possess good adhesive and lubricating properties over a wide range of temperatures and pressures; they must be stable, and they must not be corrosive.

The manufacture of grease has been described by Klomgard, Simpson and Welch, and Fusstoig. In preparing greases, a charge of fat, mineral oil, solid caustic soda or other alkali, and
water is charged into a large kettle provided with a means of heating and with some device for agitation. On heating, the fat will be saponified by the alkali, forming a soap, and the entire mixture will become fluid. On cooling and with constant stirring the paste-like gel is formed.

Various formulas for different types of greases have been published in various trade and technical journals and books. Klomgård\(^{430}\) and Fussteig\(^{432}\) have presented some formulas which are well known. Kadmur\(^{433}\) has made a comprehensive review of the literature and patents on grease manufacture. His article supplements the information contained in the book by Klomgård. Iicata\(^{434}\) has described the production of aluminum stearate greases and McLennan\(^{435}\) has described the production of barium greases. Most manufacturers of greases only reveal the nature of their greases through the patent literature.

Lawrence\(^{437}\) discusses the structure of lubricating greases and points out that soap-oil solutions may be (a) a true solution whose viscosity is but a little higher than that of the oil alone, (b) a true gel, or (c) a pseudo-gel or paste of soap crystallites suspended in oil. Calcium-base greases belong to the second class, i.e., gels, while sodium- and aluminum-base greases are believed to be pseudo-gels. The type of soap employed affects the hardness of grease at various temperatures. Lawrence expresses the belief held by many that the soaps are not dissolved by the oil on heating but that the soap-lattice opens up and the oil penetrates between the hydrocarbon chains.
The properties of the various types of greases are discussed by Klomgard, Simpson and Welch, Furstig, McLennan, and Copley. Sodium and potassium soap greases are soluble in water, have a fibrous, sponge-like texture, and have high melting points. Sodium soap greases withstand temperatures above 165°F best, and should be used where frequent replacement is difficult or apt to be delayed. Calcium soap greases have a smooth, buttery structure and tend to flow quite readily. This renders them unsuitable for use at high temperatures. These greases are water repellent and tend to seal the bearings against water. The calcium soap greases are not considered as stable as sodium soap greases over a long period of time. Aluminum soap greases are extremely tacky and have good adhesive properties. They are water resistant and stable at high temperatures. Licata claims that the presence of 5% of sodium soap or calcium soap greases will liquify aluminum soap greases. Aluminum soap greases prepared with paraffinic, asphaltic and naphthene oils increase in hardness in the order named. Barium soap greases are heat and water resistant and do not change appreciably in consistency under severe working conditions. The change in penetration with temperature of barium soap greases is comparable to the change in sodium soap greases.

Masterkov has found that the corrosion-protecting properties of mineral-oil greases may be increased by the addition of 1% of sodium soaps, but the flow properties of the greases are changed by the addition. On the other hand, the addition of free caustic, such as sodium hydroxide, lowers the corrosion-protecting properties of the grease.
Masterkov\(^{(439)}\) also claims that the presence of rosin in the grease caused corrosion on prolonged contact. This is probably due to the free abietic acid which is present. Matthews\(^{(440)}\) investigated the corrosive properties of greases and found that rosin oil or cottonseed oil in place of petroleum oils in greases was detrimental from a corrosion standpoint. Copper surfaces are readily attacked by tallow and lard, and tallow also attacks iron. The presence of uncombined tallow and lard in greases would be very detrimental if protection was desired. Borudulin\(^{(441)}\) states that the presence of free naphthenic oils in preservative oils is often corrosive as can be seen by copper turning green and steel darkening.

Wright and Lutz\(^{(442)}\) have investigated the storage stability of greases in contact with metallic surfaces. This investigation was mainly concerned with the rate of oxidation of the grease by oxygen under pressure. The results obtained gave some idea as to the probable life of the grease. Sodium soap greases appeared to have a life in storage of from three to six years as judged by these tests, but the actual life might vary considerably according to other conditions of storage.

Testing methods for determining lubricating grease characteristics have been discussed by Wright and Mills\(^{(443)}\), McConvillo\(^{(444)}\), and Georgi\(^{(445)}\).
APPENDIX I

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