

**Other  
Hydrogen  
Processes**

Several hydrogen processes have been used in addition to hydrofinishing. Hydrotreating, a more severe process, is sometimes used prior to solvent extraction. The objective is to improve the yield from the extraction process by converting some of the aromatic molecules, which would end up in the extract, into nonaromatic molecules that will remain in the raffinate. In this process, a high degree of desulfurization usually is realized, as well as a moderate degree of nitrogen removal. When this process is employed, hydrofinishing of the product oil is not needed.

Catalytic hydrodewaxing, in which the wax molecules are catalytically cracked to lower boiling products, has been proposed. While few commercial units have been built, it is likely that such units will be produced, especially for the production of low-boiling products.

# Lubrication Fundamentals

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**ADDITIVES**

Additives are chemical compounds added to lubricating oils to impart specific properties to the finished oils. Some additives impart new and useful properties to the lubricant, some enhance properties already present, while some act to reduce the rate at which undesirable changes take place in the product during its service life.

Additives, in improving the performance characteristics of lubricating oils, have aided significantly in the development of improved prime movers and industrial machinery. Modern passenger car engines, automatic transmissions, hypoid gears, railroad and marine diesel engines, high speed steam turbines, and industrial processing machinery, as well as many other types of equipment would have been greatly retarded in their development were it not for additives and the performance benefits they provide.

Additives for lubricating oils were used first during the 1920s and their use has since increased tremendously. Today, practically all types of lubricating oils contain at least one additive, and some oils contain several different types of additives. The amount of additive used varies from a few hundredths of a percent to 30 percent or more.

In addition to their primary beneficial effects, additives can have detrimental side effects, especially if the dosage is excessive or if interactions with other additives occur. It is the responsibility of the oil formulator to achieve a balance of additives for optimum performance, and to ensure by testing that this combination does not exhibit undesirable side effects. When this is achieved, it is usually unnecessary and undesirable for the oil user to add oil additive supplements.

The more commonly used additives are discussed in the following sections. Although some are multifunctional, as in the case of certain VI improvers which also function as pour point depressants or dispersants, they are discussed only in terms of their primary function.

#### **Pour Point Depressants**

These are high molecular weight polymers that function by inhibiting the formation of a wax crystal structure that would prevent oil flow at low temperatures. Two general types are used:

1. Alkylaromatic polymers adsorb on the wax crystals as they form, preventing them from growing and adhering to each other.
2. Polymethacrylates cocrystallize with wax prevent crystal growth.

The additives do not entirely prevent wax crystal growth, but rather lower the temperature at which a rigid structure is formed. Depending on the type of oil, pour point depression of up to 50 Fahrenheit degrees (28 Celsius degrees) can be achieved by these additives, although a lowering of the pour point by about 20 to 30 Fahrenheit degrees (11 - 17 Celsius degrees) is more common.

#### **Viscosity Index Improvers**

These are long chain, high molecular weight polymers that function by increasing the relative viscosity of an oil more at high temperatures than they do at low temperatures. Generally this results from the polymer changing its physical configuration with increasing temperature of the mixture. It is postulated that in cold oil the molecules of the polymer adopt a coiled form so that their effect on viscosity is minimized. In hot oil, the molecules tend to straighten out, and the interaction between these long molecules and the oil produces a proportionally greater thickening effect. *Note:* although the oil-polymer mixture still decreases in viscosity as the temperature increases, it does not decrease as much as would the oil alone.

Among the principal VI improvers are methacrylate polymers and copolymers, acrylate polymers, olefin polymers and copolymers, and styrene-butadiene copolymers. The degree of VI improvement from these materials is a function of the molecular weight distribution of the polymer.

The long molecules in VI improvers are subject to degradation due to mechanical shearing in service. Shear breakdown occurs by two mechanisms. Temporary shear breakdown occurs under certain conditions of moderate shear stress and results in a temporary loss of viscosity. Apparently, under these conditions the long molecules of the VI improver align themselves in the direction of the stress so there is less resistance to flow. When the stress is removed, the molecules return to their usual random arrangement and the temporary viscosity loss is recovered. This effect can be beneficial in that it can temporarily reduce oil friction to permit easier starting, as

when cranking a cold engine. Permanent shear breakdown occurs when the shear stresses actually rupture the long molecules, converting them into lower molecular weight materials that are less effective VI improvers. This results in a permanent viscosity loss, which can be significant. It is generally the limiting factor controlling the maximum amount of VI improver that can be used in a particular oil blend.

VI improvers are used in engine oils, automatic transmission fluids, multipurpose tractor fluids, and hydraulic fluids. They are also used in gear lubricants to some extent. Their use permits the formulation of products that provide satisfactory lubrication over a much wider temperature range than is possible with straight mineral oils alone.

### **Defoamants**

The ability of oils to resist foaming varies considerably depending on the type of crude oil, type and degree of refining, and viscosity. In many applications, there may be considerable tendency to agitate the oil and cause foaming, while in other cases even small amounts of foam can be extremely troublesome. In these cases, a defoamant may be added to the oil.

Silicone polymers used at a few parts per million are the most widely used defoamants. These materials are marginally soluble in oil, and the correct choice of polymer size is critical if settling during long term storage is to be avoided. Also, they may increase air entrainment in the oil. Organic polymers are sometimes used to overcome these difficulties with the silicones, although much higher concentrations are required.

It is thought that the defoamant molecules attach themselves to the air bubbles in the foam, producing points of weakness. The bubbles, therefore, coalesce into larger bubbles which rise more readily to the surface of the foam layer and there collapse, releasing the air.

### **Oxidation Inhibitors**

When oil is heated in the presence of air, oxidation occurs. As a result of this oxidation, the oil viscosity and concentration of organic acids in the oil both increase, and varnish and lacquer deposits may form on hot metal surfaces exposed to the oil. In extreme cases, these deposits may be further oxidized to hard, carbonaceous materials.

The rate at which oxidation proceeds is affected by several factors. As the temperature increases, the rate of oxidation increases exponentially. Greater exposure to air (and the oxygen it contains), or more intimate mixing with it, will also increase the rate of oxidation. Many materials, such as metals, particularly copper, and organic and mineral acids, may act as catalysts or oxidation promoters.

Although the complete mechanism of oil oxidation is not too well defined, it is generally recognized as proceeding by free radical chain reaction. Reaction chain initiators are formed first from unstable oil molecules, and these react with oxygen to form peroxy radicals which in turn attack the unoxidized oil to form new initiators and hydroperoxides. The hydroperoxides are unstable and divide, forming new initiators to expand the reaction. Any materials that will interrupt this chain reaction will inhibit oxidation. Two general types of oxidation inhibitors are used: those that react with the initiators, peroxy radicals and hydroperoxides, to form inactive compounds, and those that decompose these materials to form less reactive compounds.

At temperatures below 200°F (93°C), oxidation proceeds slowly and inhibitors of the first type are effective. Examples of this type are hindered (alkylated) phenols such as 2,6-ditertiary-butyl-4-methylphenol (also called 2,6-ditertiary-butylparacresol, DBPC), and aromatic amines such as N-phenyl- $\alpha$ -naphthylamine. These are used in products such as turbine, circulation, and hydraulic oils which are intended for extended service at moderate temperatures.

When the operating temperature exceeds about 200°F (93°C), the catalytic effects of metals become important factors in promoting oil oxidation. Under these conditions, inhibitors that reduce the catalytic effect of the metals must be used. These materials usually react with the surfaces of the metals to form protective coatings and for that reason are sometimes called metal deactivators. Typical of this type of additives are the dithiophosphates, primarily zinc dithiophosphate. The dithiophosphates also act to decompose hydroperoxides at temperatures above 200°F (93°C), so they inhibit oxidation by this mechanism as well.

Oxidation inhibitors may not entirely prevent oil oxidation when conditions of exposure are severe, and some types of oils are inhibited to a much greater degree than others. Oxidation inhibitors are not, therefore, cure-alls, and the formulation of a satisfactorily stable oil requires proper refining of a suitable base stock combined with careful selection of the type and concentration of oxidation inhibitor.

### Corrosion Inhibitors

A number of kinds of corrosion can occur in systems served by lubricating oils. Probably the two most important types are corrosion by organic acids that develop in the oil itself, and corrosion by contaminants that are picked up and carried by the oil.

One of the areas where corrosion by organic acids can occur is the high strength bearing inserts used in internal combustion engines. Some of the metals used in these inserts, such as the lead in copper-lead or lead-bronze, are readily attacked by organic acids in oil, as illustrated in Fig. 2-23. The corrosion inhibitors form a protective film on the bearing surfaces that prevents the corrosive materials from reaching or attacking the metal (Fig. 2-24). The film may be either adsorbed on the metal or chemically bonded to it. The additive used for this purpose is primarily zinc dithiophosphate, but other sulfur and phosphorus containing materials are also used.

During combustion in gasoline or diesel engines, certain materials in the fuel, such as sulfur and antiknock scavengers, can burn to form strong acids. These acids can then condense on the cylinder walls and be carried to other parts of the engine by the oil. Corrosive wear of rings and cylinder walls, and corrosion of crankshafts, rocker arms, and other engine components can then occur.

It has been found that the inclusion of highly alkaline materials in the oil will help to neutralize these strong acids as they are formed, greatly reducing this corrosion and corrosive wear. These alkaline materials are also used to provide detergency. See the detailed discussion in the section on Detergents and Dispersants.

### Rust Inhibitors

Rust inhibitors are usually compounds having a high polar attraction toward metal surfaces. By physical or chemical interaction at the metal surface,

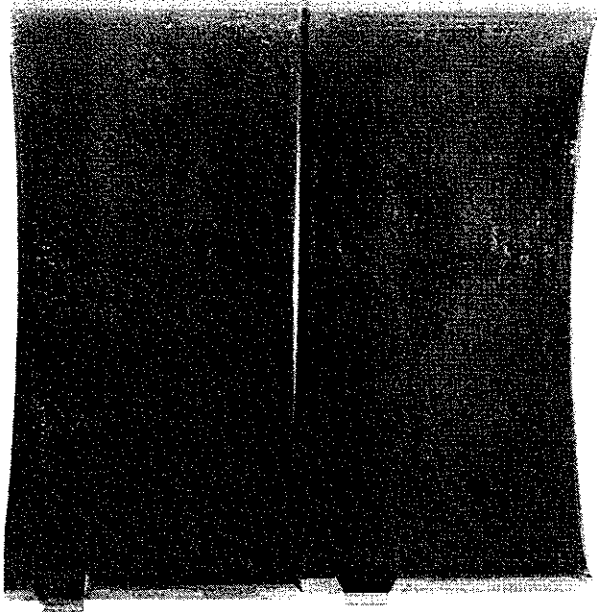


Fig. 2-23 Heavily Corroded Copper-Lead Bearing

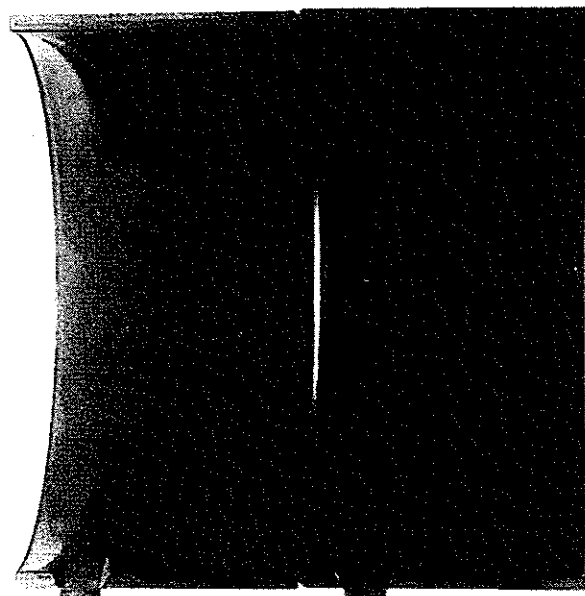


Fig. 2-24 Satisfactorily Protected Copper-Lead Bearing

they form a tenacious, continuous film which prevents water from reaching the metal surface. Typical materials used for this purpose are amine succinates and alkaline earth sulfonates. The effectiveness of properly selected rust inhibitors is illustrated in Fig. 2-25.

Rust inhibitors can be used in most types of lubricating oils, but the selection must be made carefully in order to avoid problems such as corrosion of nonferrous metals or the formation of troublesome emulsions with water. Because rust inhibitors are adsorbed on metal surfaces, an oil can be depleted of rust inhibitor in time. In certain cases, it is possible to correct this by adding more inhibitor.

### Detergents and Dispersants

In internal combustion engine service, a variety of effects tends to cause oil deterioration and the formation of harmful deposits. These deposits can interfere with oil circulation, build up behind piston rings to cause ring sticking and rapid ring wear, and affect clearances and proper functioning of critical components, such as hydraulic valve lifters. Once formed, such deposits are generally hard to remove except by mechanical cleaning. The use of detergents and dispersants in the oil can delay the formation of deposits and reduce the rate at which they deposit on metal surfaces. An essential factor with this approach is regular draining and replacement of the oil so that the contaminants in it are removed from the engine before the oil's capacity to hold them is exceeded.

Detergents are generally considered to be those chemical compounds which chemically neutralize deposit precursors that form under high temperature conditions or as the result of burning fuels with high sulfur content or other materials that form acidic combustion products. Dispersants, on the

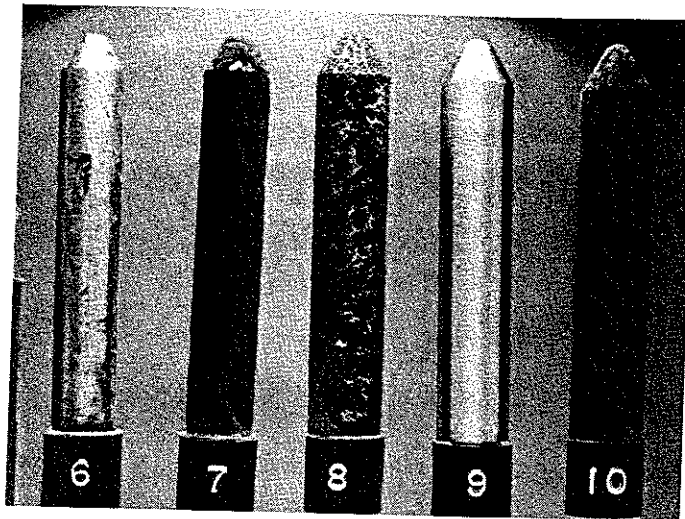


Fig. 2-25 ASTM Rust Test Specimens

other hand, are chemical compounds that disperse or suspend in the oil potential sludge forming materials, particularly those formed during low temperature operation when condensation and partially burned fuel find their way into the oil. These contaminants are removed from the system when the oil is drained. There is no sharp line of demarcation between detergents and dispersants. Detergents have some ability to disperse and suspend contaminants, while dispersants have some ability to prevent the formation of high temperature deposits.

The principal detergents used today are organic soaps and salts of alkaline earth metals such as barium, calcium, and magnesium. These materials are often referred to as metallo-organic compounds. Barium, calcium, and magnesium sulfonates, and barium and calcium phenates (or phenol sulfides) are widely used, and barium phosphonates are still used in some applications. The sulfonates and phenates may be neutral or overbased, that is, contain more of the alkaline metal than is required to neutralize the acidic components used in making the additive. Overbased materials are widely used in diesel engine oils to neutralize the strong acids formed from combustion of the sulfur in the fuel. This neutralization reduces corrosion and corrosive wear and minimizes the tendency of these acids to cause oil degradation.

Overbased materials are generally not used at as high concentration in gasoline engine oils where the fuel sulfur is much lower, but are usually included to help reduce corrosion in low temperature operation. Both neutral and overbased materials also act to disperse and suspend potential varnish forming materials resulting from oil oxidation, preventing these materials from depositing on engine surfaces.

Metallo-organic detergents, on combustion, leave an ashy residue (see Sulfated Ash). In some cases, this may be detrimental in that the ash can contribute to combustion chamber deposits. In other cases, it may be beneficial in that the ash provides wear resistant coatings for surfaces such as valve faces and seats.

Typical dispersants (also called polymeric dispersants and ashless dis-

persants) in use today are described as polymeric succinimides, olefin/ $P_2S_5$  reaction products, polyesters, and benzylamides. These are based on long chain hydrocarbons which are acidified and then neutralized with a compound containing basic nitrogen. The hydrocarbon portion provides oil solubility, while the nitrogen portion provides an active site that attracts and holds potential deposit forming materials to keep them suspended in the oil.

While the primary use of detergents and dispersants is in engine oils, increasing quantities of them are being used in products such as automatic transmission fluids and circulation oils for high temperature service. In these applications, the detergents and dispersants help to prevent the deposition of lacquer and varnish resulting from oil oxidation, and in this way supplement the effects of the oxidation inhibitors.

### **Antiwear Additives**

Antiwear additives are used in many lubricating oils to reduce friction, wear, and scuffing and scoring under boundary lubrication conditions, that is, when full lubricating films cannot be maintained. As the oil film becomes progressively thinner due to increasing loads or temperatures, contact through the oil film is first made by minute surface irregularities or asperities. As these opposing asperities make contact, friction increases and welding can occur. The welds break immediately as sliding continues, but this can form new roughnesses through metal transfer, and also form wear particles which can cause scuffing and scoring. Two general classes of materials are used to prevent metallic contact, depending on the severity of the requirements.

**Mild Wear and Friction Reducing Additives** These compounds, sometimes called boundary lubrication additives, are polar materials such as fatty oils, acids, and esters. They are long chain materials that form an adsorbed film on the metal surfaces with the polar ends of the molecules attached to the metal and the molecules projecting more or less normal to the surface. Contact is then between the projecting ends of the layers of molecules on the opposing surfaces. Friction is reduced, and the surfaces move more freely relative to each other. Wear is reduced under mild sliding conditions, but under severe sliding conditions the layers of molecules can be rubbed off so that their wear reducing effect is lost.

**Extreme Pressure Additives** At high temperatures or under heavy loads where more severe sliding conditions exist, compounds called extreme pressure (EP) additives are required to reduce friction, control wear, and prevent severe surface damage. These materials function by chemically reacting with the sliding metal surfaces to form relatively oil insoluble surface films. The kinetics of the reaction are a function of the surface temperatures generated by the localized high temperatures that result from rubbing between opposing surface asperities, and breaking of junctions between these asperities.

Even with extreme pressure additives in the lubricant, wear of new surfaces may be high initially. In addition to the normal break-in wear, nascent metal (freshly formed, chemically reactive surfaces), time, and temperature are required to form the protective surface films. After the films are formed, relative motion is between the layers of surface films rather than the metals. The sliding process can lead to some film removal, but replacement by fur-

ther chemical reaction is rapid so that the loss of metal is extremely low. This process gradually depletes the amount of EP additive available in the oil although the rate of depletion is usually slow. Thus, there will be sufficient additive left to provide adequate protection for the metal surfaces.

The severity of the sliding conditions dictates the reactivity of the EP additives required for maximum effectiveness. The optimum reactivity occurs when the additives minimize the adhesive or metallic wear without leading to appreciable corrosive or chemical wear. Additives that are too reactive lead to the formation of excessively thick surface films which have less resistance to attrition, so some metal is lost by the sliding action. Since a particular EP additive may have different reactivity with different metals, it is important to match additive metal reactivity to the additives not only with the severity of the sliding system but also with the specific metals involved. For example, some additives that are excellent for steel-on-steel systems may not be satisfactory for bronze-on-steel systems operating at similar sliding severity because they are too reactive with the bronze.

Another important function of EP additives is that, because the chemical reaction is greatest on the asperities where contact is made and localized temperatures are highest, they lead to polishing of the surfaces. The load is then distributed more uniformly over a greater contact area which allows for a reduction in sliding severity, more effective lubrication, and a reduction in wear.

Extreme pressure agents are usually compounds containing sulfur, chlorine, or phosphorus, either alone or in combination. The compounds used depend on the end use of the lubricant and the chemical activity required in it. Sulfur compounds, sometimes with chlorine or phosphorus compounds, are used in many metal cutting fluids. Sulfurphosphorus combinations are used in some industrial gear lubricants, and in special cases sulfur-chlorine-lead compounds are used in some automotive gear lubricants. The major amounts of both automotive and industrial gear lubricants are now formulated with sulfur-phosphorus compounds. These materials provide excellent protection against gear tooth scuffing and have the advantages of better oxidation stability, lower corrosivity, and often lower friction than other combinations that have been used in the past.

### PHYSICAL AND CHEMICAL CHARACTERISTICS

There are a multitude of physical and chemical tests which yield useful information on the characteristics of lubricating oils. However, the quality or the performance features of a lubricant cannot be adequately described on the basis of physical and chemical tests alone. Thus, major consumers of lubricating oils, such as military purchasing agencies and many commercial consumers, include performance tests as well as physical and chemical tests in their purchase specifications. Physical and chemical tests are of considerable value in maintaining uniformity of products during manufacture. Also, they may be applied to used oils to determine changes that have occurred in service, and to indicate possible causes for those changes.

Some of the most commonly used tests for physical or chemical properties of lubricating oils are outlined in the following sections, with brief ex-