

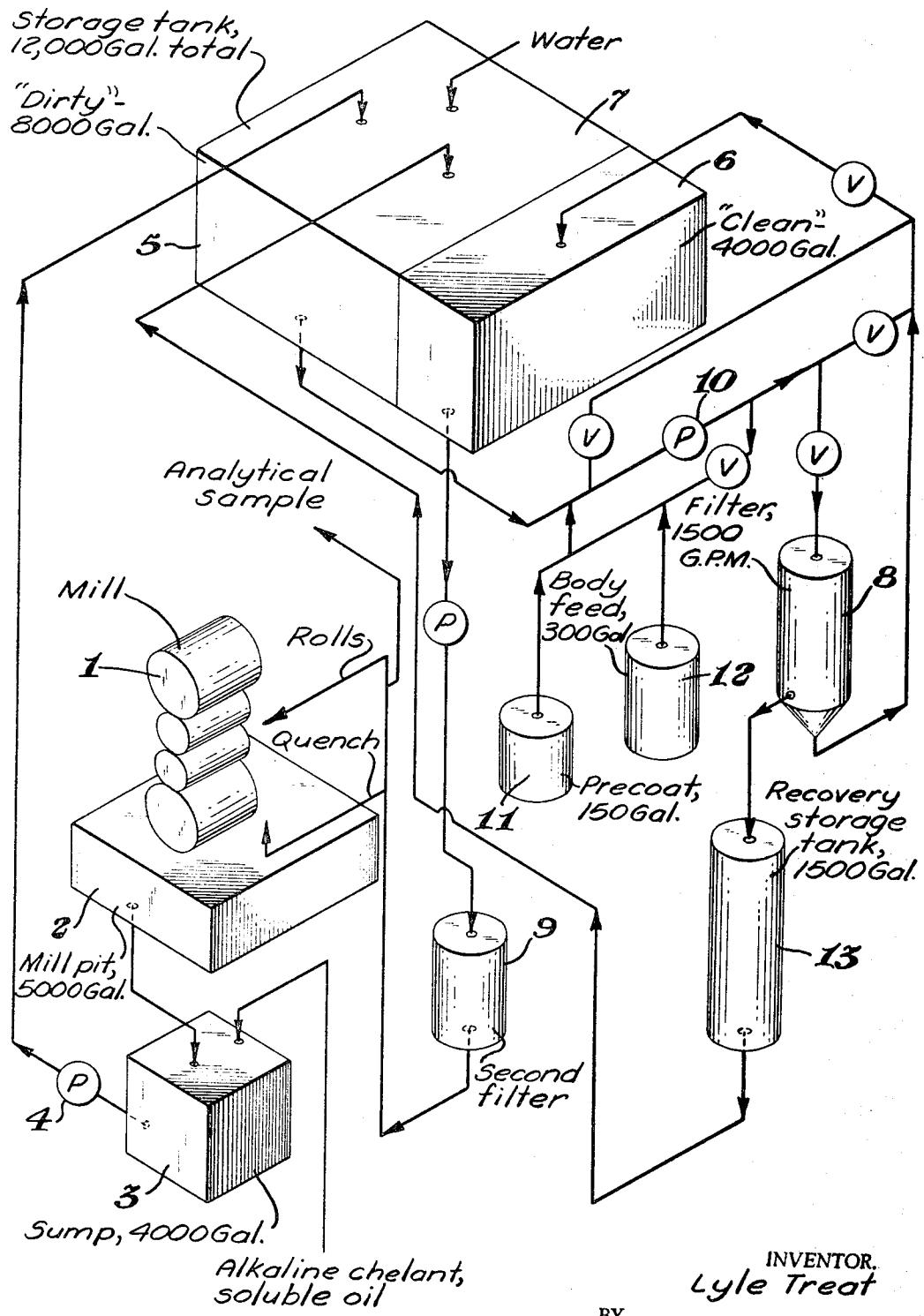
Nov. 5, 1968

L. TREAT

3,408,843

## LUBRICANT-COOLANT EMULSION STABILIZATION AND REUSE

Filed Oct. 26, 1966



INVENTOR.  
*Lyle Treat*

BY

Edward E. Schilling  
ATTORNEY

1

3,408,843

## LUBRICANT-COOLANT EMULSION STABILIZATION AND REUSE

Lyle Treat, Ferguson, Mo., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware  
Continuation-in-part of application Ser. No. 443,528, Mar. 29, 1965. This application Oct. 26, 1966, Ser. No. 589,730

8 Claims. (Cl. 72—42)

### ABSTRACT OF THE DISCLOSURE

A lubricant-coolant oil-in-water emulsion used in the shaping of a metal is stabilized and kept filterable by periodically adding polycarboxylic acid chelating agent, such as a polyacetic acid, or salt thereof, in the requisite amount to adjust and maintain the hardness level of the emulsion below about 400 p.p.m. (expressed as  $\text{CaCO}_3$ ) and the pH value in the range of about 5 to 11. Preferably the hardness level is maintained in the range of about 25 to 400 p.p.m. and the emulsion is also filtered to remove solid particles larger than about 0.5 to 10 microns maximum dimension.

The present application is a continuation-in-part of prior application Ser. No. 443,528, filed Mar. 29, 1965, now abandoned.

The invention relates to the hot or cold working, cutting or other shaping of metal in any operation wherein there is used a flowing lubricant-coolant oil-in-water emulsion which is recycled and reused. The invention also relates to the composition of such emulsions as well as a method for improving such emulsions.

For the purposes of the following description and the appended claims: (1) aluminum and its alloys containing at least 70 percent by weight of aluminum are herein-after referred to as aluminum; (2) magnesium and its alloys containing at least 70 percent by weight of magnesium are herein-after referred to as magnesium; (3) copper and its alloys containing at least 50 percent by weight of copper are herein-after referred to as copper; (4) iron and its alloys containing at least 75 percent by weight of iron are herein-after referred to as "ferrous metal"; (5) the operations of rolling, working, drawing, cutting, milling, scalping, drilling, or grinding and the like of metals are herein-after referred to variously, as "method of shaping a metal," metal shaping, and the like; and (6) the phase flowing lubricant-coolant oil-in-water emulsion is intended to encompass such emulsions which are sprayed on the workpiece or tool.

In methods of shaping metals in which lubrication is required it has become common to use an oil-in-water emulsion in place of prior used non-aqueous hydrocarbon lubricants. For example, in rolling a metal such as aluminum, magnesium, or steel through steel work rolls it is usual to use an oil-in-water emulsion to flood the rolls and the work stock. The emulsion serves the dual functions of both coolant and lubricant. As a coolant in cutting operations, the emulsion helps to control the temperature of the cutting tool. As a coolant in other shaping operations, for example, in rolling, the pattern of distribution of the emulsion on the work rolls is regulated to control the temperature gradient of the rolls transversely to the work stock and hence the shape of the rolls is controlled. The rate of flow of the emulsion onto the metal being shaped regulates the temperature thereof during the various stages of shaping.

As a lubricant, the emulsion serves: (1) to control the frictional forces existing between the workpiece and the

2

work tool; (2) to promote the development of desired tool coatings during the shaping process, e.g., roll-coating during rolling; and (3) to prevent excessive transfer of metal from the workpiece to the tool or from the tool to the workpiece, e.g., between the rolls and the workpiece as in rolling operations.

Typical lubricant-coolant oil-in-water emulsions that have been used for metal shaping operations such as rolling or cutting have consisted essentially of from about 0.5 to 20 percent by weight of an oil in water, the oil being a mixture referred to in the trade as neat soluble oil or soluble oil. Such neat soluble oil is widely sold as a concentrate containing, generally, about 70-90 percent by weight of a base oil, such as a light mineral oil, from about 1 to 20 percent by weight, based on said neat soluble oil, of one or more anionic and/or nonionic oil-in-water emulsifying agents and the balance substantially water. For most metal shaping operations, the neat soluble oil must also contain from about 0.5 to 15 percent by weight of lubricity additives such as long chain fatty acids and salts or esters thereof, e.g., alkanolamine soaps, or, esters such as butyl stearates which serve as extreme pressure agents. Such emulsions are made up conventionally by admixing one of the commercially available substantially water-free concentrates with water. The commercial concentrates usually contain up to 0.5 percent by weight of a bactericide and from about 0.5 to 5 percent by weight of a coupling agent, i.e., a substance which stabilizes the concentrate during storage prior to use.

The composition of the neat soluble oil itself forms no part of the present invention. The method and composition of the invention are usable with substantially all of the commonly known and used commercially available neat soluble oils, without modification of the soluble oil per se.

Suitable commercial compounded oils, i.e., soluble oils, include, for example, Solvac 1535G, Prosol 44 and Prosol 66 supplied by Socony Mobil Oil Company, Rollex A supplied by the Shell Chemical Company, Majestic #101 supplied by Fiske Brothers Refining Company, RolKleen #53 supplied by the D. A. Stuart Oil Company, Ltd., A-100 supplied by Far Best, W.S. 51821 supplied by the Humble Oil Company and Tandemol C86 and Tandemol K87 supplied by E. F. Houghton and Company.

A typical neat soluble oil that is commercially available has the following general composition, by weight:

	Percent
50 Light mineral oil	83
Lubricity additives	11
Emulsifiers	4
Coupling agents	0.5
Bactericide	0.5
55 Detergent	1

The base oil used in making up a neat soluble oil generally is selected from a light hydrocarbon or light hydrocarbon mixture having a viscosity of about 40 to 200 Saybolt Universal seconds (SUS) at 100° F. However, other lubricious materials such as fatty oils, e.g., palm oil, or synthetic materials, e.g., palm oil substitutes, are also used as a base oil in making up soluble oil. Such other lubricious materials may have viscosities as high as about 850 SUS.

For the purposes of the following description and the appended claims, the term base oil is understood to encompass the light hydrocarbon or hydrocarbon mixtures recognized as light mineral oils, in addition to lubricious materials including vegetable oils, such as palm oil, animal fats, such as lard oil, and palm oil substitutes and the equivalents thereof, e.g., polyglycols and ethers and esters

thereof, selected from those which are non-staining of the metal being shaped.

Suitable anionic oil-in-water emulsifiers used in sufficient amount to emulsify the base oil include, for example: (1) alkylaryl sulfonates such as the higher alkylbenzene sulfonates wherein higher alkyl means an alkyl group having at least 8 carbon atoms, e.g.,  $C_{12}H_{25}C_6H_4SO_3Na$ ; (2) fatty alkyl sulfates such as  $CH_3(CH_2)_{10}OSO_3Na$ ; (3) the sulfonated fatty amines such as  $C_{17}H_{33}CON(CH_3)C_2H_4SO_3Na$ ; (4) the alkali metal salts of sulfonated fatty acids; and the like. The other alkali metal salts of these compounds and the triethanolamine salts are equivalents of the sodium salts described above. The alkanolamine soaps of long chain fatty acids are particularly suitable e.g., the diisopropanolamine, diethanolamine or monoethanolamine salts of oleic acid, palmitic acid or stearic acid, the salts being useful singly or as mixtures.

Suitable nonionic oil-in-water emulsifiers include the nonionic ethers such as those derived from alkylphenols and ethylene oxide, e.g.,  $C_8H_{17}C_6H_4OC_2H_4(OC_2H_4)_xOH$  wherein  $x$  has a value of 9 to 14 or more, the primary alcohol-ethylene oxide adducts, and the secondary alcohol-ethylene oxide adducts.

When one of the described oil-in-water emulsions is placed in service in metal shaping operations it tends to work well initially both as a coolant and as a lubricant, although it is commonly observed that the metal surface obtained in metal shaping operations is improved after several days of using the emulsion. With continued recycling and reusing, the emulsion ordinarily accumulates solid particulate matter including metal fines, metal oxide particles, oxidized oils, soil particles and general air-borne industrial contamination. In addition, hydraulic oils and bearing lubricants occasionally enter the emulsion as a result of accidental leakage and are collectively referred to as tramp oil. As a result of such contamination and also as a result of general use of the emulsion the emulsion begins to break and the droplets of the oil phase agglomerate into larger droplets some of which coalesce sufficiently to provide a substantial quantity of continuous free oil phase.

Separation of free oil, i.e., base oil, from the emulsion affects the lubricity properties of the lubricant-coolant in a manner adverse to rolling operations leading to refusal of the mill, in rolling operations, to accept the workpiece being fed into the rolls unless the rolls are set for only a small reduction of the workpiece. This seriously reduces the percent of reduction that can be achieved per pass. Sometimes the mill will not accept the work piece unless the rolls are set for zero reduction. In cutting or grinding operations, excessive lubricity may reduce the effectiveness of the cutting or grinding tool. The excess continuous free oil phase can also plate out on the work piece in non-cutting shaping operations such as rolling, and lead to harmful staining problems during subsequent processing such as heat treating. Similar harmful effects are observed regardless of whether the continuous free oil phase comes from the breakdown of the emulsion or the accumulation of tramp oil which is neither emulsified nor removed from the system during recycling.

For the purposes of the present invention, an emulsion which contains no more than about 0.2 percent by weight of continuous free oil phase is considered to be free of such free oil phase.

The accumulation of solid particulate matter adversely affects the success of shaping operations such as rolling. The particulate matter tends to become embedded in the metal surface leading to undesirable surface appearance. Embedded particulate matter interferes with surface treatments such as anodizing or coating. In the past the foregoing problems have necessitated skimming off some of the floating impurities from the emulsion and/or settling solids as a sludge on the bottom of large settling tanks. This has not been entirely successful because the removal is not nearly thorough enough. Skimming is also disad-

vantageous because some good emulsion is removed with the impurities and as a consequence the addition of make-up soluble oil is necessary. Some operators have tried filtering the lubricant-coolant emulsion but this has not been successful for any extended period because of blocking of the filter. All of the causes of blocking of the filter are not understood but it is believed that contributing factors are the tendency of the continuous free oil phase to accumulate on the filter media thus blanking off or blocking further passage of both aqueous phase and droplet size oil phase through the filter also, the formation and accumulation of polyvalent metal soaps in the emulsion. Only filters which pass relatively large particles have remained operable for long periods, and these filters are relatively ineffective. In most instances, operators have simply discarded the entire batch of emulsion after 3 to 6 weeks or less of steady use. A few systems employing a large reservoir of emulsion have operated for somewhat longer periods. In the case of rolling mills this involves a substantial quantity of emulsion.

Typical industrial emulsion systems vary in size from perhaps 5,000 to 10,000 gallons or less for smaller cutting or grinding operations to systems as large as 100,000 to 500,000 gallons for large rolling mills, some of which require the circulation of 1,000 to 10,000 gallons of emulsion per minute to one or more mill stands.

It is therefore a principal object of the present invention to provide an improved method for shaping metal in which there is employed a lubricant-coolant oil-in-water emulsion which is recycled and reused.

Another object of the invention is to provide a method of stabilizing and reusing a lubricant-coolant oil-in-water emulsion in metal shaping operations.

Another object of the invention is to provide a method of removing particulate matter and eliminating or reducing continuous free oil phase from lubricant-coolant oil-in-water emulsion, apart from a normal level of about 0.2 percent by weight of such oil phase, which is not detrimental in effect.

A further object of the invention is to provide a method of increasing the service life of lubricant-coolant oil-in-water emulsions used in the shaping of metal.

Yet another object of the invention is to provide an improved lubricant-coolant oil-in-water emulsion for use in metal shaping operations.

These and other objects and advantages of the present invention will be more clearly understood by those skilled in the art upon becoming familiar with the following description and the illustrative examples.

It has been discovered that a conventional rolling or cutting oil emulsion is improved by the addition thereto of an alkaline alkali metal or ammonium or amine salt of a polycarboxylic acid chelating agent in an amount sufficient to chelate calcium, magnesium, aluminum, heavy metal or other polyvalent metal ions present or accumulating in such an emulsion whereby the hardness content, expressed as  $CaCO_3$ , is reduced below about 400 p.p.m., and the emulsion pH is brought into the range of about 5 to 11. Where foaming is a problem it is much preferred to bring the hardness content to about 25 to 400 p.p.m. In addition to the initial adjustment, the maintenance of a controlled level of hardness content below about 400 p.p.m., expressed as  $CaCO_3$  and a pH in the range of about 5 to about 11 is essential. Such management of the emulsion substantially prevents oil separation therefrom and has the following further important effects: (a) the emulsion is stabilized so that it can be filtered through a mechanical filter capable of removing solid particulate matter larger than 10 to 20 microns size, and preferably, larger than 1 micron, such as a filter provided with a siliceous pre-coating; (b) solid particulate contamination such as dirt, metal fines, and metal oxide particles are readily removed on the filter without premature filter blank off problems; (c) light viscosity tramp oils leaking into the system are substantially emulsified thus minimiz-

ing the quantity of free oil phase; and (d) oxidized oils and reaction products thereof are removed on filtration.

An important aspect of the present invention is the discovery that the particle diameter of the globules of emulsified oil is at least partly a function both of pH and hardness content of the emulsion, the nature and concentration of the emulsifying materials present being also controlling factors. This role of hardness had not been appreciated heretofore. Both calcium and magnesium hardness are generally derived in part from the water used to make up the emulsion. Large quantities of water are frequently and periodically added in many metal shaping operations to replace losses due to evaporation bringing about the addition of substantial amounts of calcium and magnesium hardness. Calcium, and to some extent magnesium ions, also enter the emulsion from concrete mill pits or sumps and storage tanks in which the emulsion is received or stored. Especially in the case of magnesium and aluminum, the work piece employed is a substantial source of magnesium and/or calcium and/or aluminum ions. These appear to be the main sources which provide for a build-up of hardness content in the emulsion, particularly calcium and magnesium, as the emulsion is recycled and reused.

While substantially all of the hardness ions could be chelated with the chelating agents employed in the invention, if desired, foaming of the emulsion during pumping and spraying operations tends to be a problem in most operations when the hardness level falls too low. Where foaming tends to be excessive and undesired, a hardness level in the range of 100 to 200 p.p.m. expressed as  $\text{CaCO}_3$  is preferred; where foaming is less of a problem, a hardness level in the range of 25 to 100 p.p.m. is preferred.

The metals which may be rolled or shaped according to the present invention include aluminum, copper, ferrous metal, such as steel, and magnesium. These metals may be shaped cold, or at temperatures as high as about  $1050^\circ \text{ F.}$ , using the emulsion of the invention.

The chelating agents used in the method of this invention are the alkali metal or ammonium or amine salts of polycarboxylic acids, including citric acids, tartaric acid, the alkylene amino polyacetic acids, and mixtures of any of the said salts of such polycarboxylic acids. The alkylene amino polyacetic acids include ethylenediamine-tetraacetic acid and its well-known homologs and analogs such as N-hydroxyethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, nitrilotriacetic acid, N-2-hydroxyethylimino diacetic acid, cyclohexanenediaminetetraacetic acid and their obvious equivalents. The amine salts or soaps referred to include particularly the salts made from one of these polycarboxylic acids and any one of ethanolamine, diethanolamine, and triethanolamine.

The reused lubricant-coolant oil-in-water emulsion ordinarily employed according to the invention in the shaping of a metal wherein the work piece is contacted with a flowing stream of said emulsion comprises:

(1) from about 1 to about 20 percent by weight of a neat soluble oil; (2) polycarboxylic acid chelant spent with metal ions selected from the group consisting of calcium, magnesium, aluminum, and heavy metal ions; (3) up to 400 p.p.m., unchelated hardness, expressed as  $\text{CaCO}_3$ ; and (4) the balance substantially water. If desired, the emulsion may also contain (1) an anti-foaming agent and/or (2) a corrosion inhibitor and/or (3) an additional lubricity agent, such additions not exceeding a total of about 5 percent by weight.

The reused emulsion is further characterized by having a pH in the range of about 5 to about 11, but preferably 7 to 10, by the dispersed oil being in the form of globules having an average globule diameter in the range of about 1 to 25 microns and substantially no globules having a diameter exceeding about 50 microns, by a selected globule diameter being readily maintainable, by the emulsion being readily filterable through a mechan-

ical filter capable of removing solid particles larger than 10 to 20 microns size but preferably particles larger than 0.5 to 1 micron, and by the emulsion being (1) substantially free of solid particles larger than about 10 to 20 microns but preferably no larger than 0.5 to 1 micron and (2) free of more than about 0.2 percent of a free oil phase.

If the reused emulsion is a tight emulsion designed for reversing mill work and cutting operation, for example, the reused emulsion is also further characterized by the dispersed base oil being in the form of globules having an average globule diameter in the range of about 1 to 2 microns and substantially no globules having a diameter exceeding about 5 microns.

15 If the reused emulsion is a loose emulsion designed for use with a tandem mill or other operations where more lubricity is required or tolerated, the dispersed oil phase is in the form of globules having an average globule diameter in the range of about 2 to 5 microns with substantially no globules larger than about 15 microns.

20 If the reused emulsion is a coarse emulsion designed for cold rolling steel or aluminum, the dispersed oil phase is often in the form of globules having an average globule diameter in the range of about 5 to 20 microns with substantially no globules larger than about 50 microns diameter.

25 Each of tight, loose and coarse emulsions are readily filterable when treated and maintained according to the invention. An important aspect of the invention is the provision for maintenance and control of globule diameters while avoiding emulsion breakage. Even the normally metastable emulsions are maintainable.

30 Tight emulsions are obtained and maintained upon pumping, mixing or otherwise thoroughly agitating the emulsion and further filtering the emulsion under conditions in which the concentration of unchelated hardness is below about 100 p.p.m. Coarse emulsions, on the other hand, tend to arise and be maintained under conditions wherein the amount of unchelated hardness is substantially above 200 parts per million. The basic tendency of the emulsion to exhibit fine or coarse globules is dependent upon the materials used to make up the compounded soluble oil concentrate. It is to be understood that making up and maintaining an emulsion according to the present invention provides an effect that is superimposed upon

35 the basic nature of the preselected emulsion. The net result is that the emulsion size moves to a dynamically stable size and is controllably maintainable at such dynamically stable size using the composition and method of the invention, i.e., upon maintaining the unchelated hardness below about 400 p.p.m. and the pH in the range of 5 to 11, a soluble oil emulsion will reach a dynamically stable globule size averaging about 1 to 25 microns diameter with substantially no globules larger than 50

40 microns diameter.

45 In carrying out the process of the invention an emulsion is made up generally from water and a commercial neat soluble oil of the type described hereinabove. If desired, the emulsion may be made up from the individual components.

50 The alkali metal or ammonium or amine salt of polycarboxylic acid chelating agent used according to the invention is added to the water employed in making up the emulsion or the chelating agent may be added to the diluted emulsion in any convenient form, i.e., as a solution, slurry, or dry particulate solid. In any event the chelating agent, usually in the form of a 20 to 40 percent by weight aqueous alkaline solution, is added in the requisite amount to bring the hardness level and the pH into the ranges indicated hereinabove. Generally, the water employed or the finished emulsion, as the case may be, is analyzed in order to determine the needed quantity of chelating agent solution.

55 The completed emulsion is then placed in service in metal shaping operations. Generally, clean emulsion is

circulated from clean storage to the workpiece where it is used. The emulsion flowing off the workpiece and off the tool or mill is collected as in a sump where some of the particulate matter present settles out. The emulsion may be allowed to settle further in a system with a large inventory of emulsion, but in general, the emulsion is more or less in constant circulation. A brief quiet period in a "dirty" tank is advantageous in the collection and removal of tramp oils before subsequent filtration. Thereafter on occasional cycles the emulsion is sampled for analysis, and hardness level and pH are adjusted by the addition of the indicated requirements of alkaline solution of chelating agent. The emulsion is then pumped to clean storage; if desired, the addition of chelating agent solution may be made to the emulsion in the clean storage vessel.

More preferably the emulsion after settling in dirty storage is filtered before sampling, adjusting the hardness and pH levels, and pumping to clean storage. Filtering is conveniently and effectively carried out with most any mechanical filter, such as one employing a filter paper or membrane, and especially a filter using a pre-coat of a siliceous material such as diatomaceous earth. The filter must be capable of removing fine particulate matter, preferably all matter coarser than one micron size. A very effective form of filter for handling large volumes of emulsion rapidly is a tube-type filter using an array of cylindrical tubes formed of wire mesh made of Monel metal having mesh openings in the range of 0.004 inch to 0.008 inch and coated with a filter aid such as Celite 545 diatomaceous earth of which about 80 percent of the particles are finer than about 40 microns. The filter aid forms a filter cake on each tube that retains solids greater than about 1 micron in shortest dimension. The filter tube extends into the emulsion to be filtered providing a very extensive filtering surface within a compact zone.

The clean emulsion remains in clean storage until use when the cycle commences again with the pumping of the lubricant-coolant emulsion to the metal shaping operation. Normally, the retention in clean storage is brief, being of the order of 5 to 30 minutes unless a very large inventory of emulsion is used. Lubricant-coolant emulsion so-handled and maintained remains stable and usable throughout many, many cycles completed during the space of from several months to several years and usually during at least 6 months or more of steady use.

The following examples serve to illustrate the invention and not to limit the scope thereof.

#### EXAMPLE 1

This example will best be understood with reference to the accompanying drawing on which there is depicted a schematic flow diagram for an 18,000 gallon emulsion system. In the diagram there is shown the flow pattern of lubricant-coolant emulsion from the mill rolls of a rolling mill, through the conditioning equipment, and back to the rolls in a commercial aluminum rolling mill. In the drawing, the reference numeral 1 refers generally to an 84 inch wide 4-high reversing hot mill. In its operation, 5,000-pound slabs of aluminum ingot (not shown) were rolled from an initial thickness of approximately 14 inches to various gauges down to a final gauge less than about  $\frac{1}{4}$  inch thick, the metal at the final pass having the form of either sheet or plate. Product from this mill must be suitable either as a final product, or as re-roll stock to be further processed before use.

During the rolling operation, a flood lubricant-coolant emulsion, as described above, was applied to the work-rolls through a system of spray-nozzles (not shown). The relative distribution of coolant across the width of the rolls was regulated by adjusting the flow through the various nozzles provided. By regulating the degree of cooling of the work rolls from their centers to their edges,

the relative amount of roll clearance from the centers to the edges of the rolls is controlled and thereby the flatness of the product is maintained. The emulsion temperature was in the preferred 120°-130° F. range as it is initially on the mill rolls.

Provision was also made for directing a stream of coolant emulsion onto the product itself (not shown) as it left the rolls and before it was coiled or cut in pieces and stacked. Cooling of the metal product at this stage is often essential to the prevention of surface damage to the finished product.

In this case, such provision consisted in having the lubricant-coolant emulsion, as it left the work rolls, cascade down over the rolled metal emerging from the mill. The emulsion was carefully removed from the rolled metal by jets of air (not shown) that blew it off before the metal moved very far from the mill. Careful removal is important, for residual coolant on the product may result in staining of its surface.

The coolant then passed by gravity into a mill pit 2, a 5,000 gallon reservoir beneath the mill, and thence to a 4,000 gallon sump 3. These two reservoirs serve primarily as collection points for coolant, but a valuable secondary function is that of foam storage. Foam that is generated at the mill, particularly in spray-quench operations, needs time to break down, and these reservoirs provide a storage capacity to afford this time. Foam breakdown may be assisted by the addition of appropriate antifoaming agents to the mill pit contents.

Sump pumps 4 then carried the lubricant-coolant emulsion to a 12,000 gallon storage tank 5 which is divided into a 4,000 gallon clean compartment 6, and an 8,000 gallon dirty compartment 7. From the sump, the emulsion was directed first to dirty compartment 7. From there it was pumped through a mechanical filter 8 precoated with Celite 545 diatomaceous earth, and returned to the clean compartment 6. The filter has a capacity of 1,500 gallons per minute, a rate that is faster than the normal mill-demand rate. Therefore, while the clean and dirty compartments of the storage tank communicate with each other, normally the flow not needed in the metal shaping operations was directed from the clean compartment 6 to the dirty compartment 7. During temporary periods, for example, when the mechanical filter 8 was being back-washed, the reverse flow took place, i.e., from the dirty compartment to the clean compartment. Therefore, a secondary coarse strainer filter 9 was provided in the system to remove particles large enough to clog the spray nozzles used at the mill. From the clean compartment 6 the coolant ordinarily flowed through such secondary filter 9 on its way to the mill.

This prevented gross contaminant particles being carried along with the coolant and plugging the spray nozzles (not shown) during such temporary periods when the mechanical filter was being by-passed.

The mechanical filter was a tube-type filter, containing about 750 tubes of woven Monel-wire mesh. Each tube was 1-inch in diameter and 3 feet long. The wire diameter was 0.011 inch. The mesh openings have maximum dimensions of 0.006 inch to 0.008 inch while the average openings are 0.004 inch x 0.006 inch.

At the start-up of filtration after back-washing the mechanical filter, the filter tubes were precoated with Celite 545 diatomaceous earth, a filter aid of which about 80 percent of the particles are finer than about 40 microns. The pre-coat or filter cake formed on each tube retained solids greater than one micron in diameter. The pre-coat was introduced into the suction side of the filter pump 10 from a 150 gallon tank 11 in the form of a suspension containing 100 pounds of filter aid and the balance water. One-half of the contents of this tank were used to pre-coat the filter; thus 50 pounds of filter aid formed the initial cake. The porosity of the filter was controlled during the useful life of the filter cake by periodic controlled additions of filter aid, as well understood in the art. These subsequent additions, were made from a suspension

known as body feed, which consisted of about 50 pounds of filter aid and the balance being 300 gallons of water. Normally, body feed was metered in during approximately three seconds out of each minute at a rate sufficient to provide about 50 pounds of filter aid during each 24-hour period. In addition to the original 50 pound pre-coat, the filter can handle an additional 200 pounds of body feed. Thus, under normal operating conditions, about five days of filter operation were attainable between back-washes. When an unusual condition occurred, such as excessive leakage of tramp oils into the system, or greater dirt load from rolling certain alloys, a faster rate of body feed was employed to avoid excessive pressure-drop build-up across the filter. In this case, the cycle between back-washes was shortened.

The back-wash operation requires about 35 minutes. During back-wash, coolant from the filter vessel was discharged into the 1,500 gallon recovery storage tank 13. The entire recovery filter cycle takes about 7 hours. Filtration of the back-wash to retain used filter aid solids for waste disposed was accomplished advantageously by making use of a cloth-type filter or equivalent (not shown).

Additions to the emulsion system were made at the following places: (1) replacement of water lost by evaporation and drag-out on the product was introduced directly into the dirty compartment 7 (up to 7,000 gallons per day). De-ionized water was used to minimize introduction of magnesium and calcium ions into the system. On occasion, ordinary hard water was used, i.e., some hardness was deliberately added to minimize foaming; (2) soluble oil and chelating agent were added at the sump 3; (3) anti-foam agents, if needed, were introduced at the mill pit 2.

Samples for analytical control were removed after the final filtering just before the lubricant-coolant emulsion was pumped to the mill.

The composition of the lubricant-coolant emulsion was maintained in the following manner. The oil phase of the emulsion consisted of 4.5 to 6.0 weight percent of a light oil, having a viscosity, at 100° F., of 100-200 SUS, emulsified in water with one or more anionic and/or non-ionic emulsifiers as described above. The emulsion was made up with water. To the resulting emulsion, there was added an aqueous solution of an alkaline chelant. The quantity of such alkaline chelating agent used was such as to bring the hardness of the aqueous phase of the emulsion within a range of 100-200 p.p.m., expressed as  $\text{CaCO}_3$ , and the pH within a range of 9 to 10, to give the emulsion the desired properties of stability and lubricity. When the hardness of the emulsion approached 200 p.p.m., more chelating agent was added.

The following analytical control tests were routinely executed to determine times of addition of additives needed to maintain the desired properties of the lubricant-coolant emulsions.

1. *Percent soluble oil.*—This test gives the concentration of oil in the emulsion. The concentration is determined by breaking a sample of the emulsion with acid, centrifuging the broken emulsion, and measuring the oil layer. Adjustment of the oil concentration to the desired range is accomplished by the addition of "neat" soluble oil or de-ionized water.

2. *Percent free oil.*—This is determined by centrifuging a sample of the emulsion for a predetermined time and measuring the oil layer. Generally one expects only a trace to be visible. Preferably, when the free oil level reaches from 0.2 to 0.4 percent, chelant salt is added to correct the problem. When the free oil level reaches a level of 0.6 percent by weight, mill entry problems are encountered because of excess lubricity.

3. *Hardness.*—The concentration of polyvalent metal ions, such as magnesium, calcium, and aluminum ions, was maintained in the range of 100-200 p.p.m., expressed as calcium carbonate. Additions of chelant salt were made

to prevent build-up above this range. Addition of "hard" make-up water was employed to increase hardness on a few occasions when the hardness fell below the desired range.

5 4. *Filter time.*—This test measures the time for one gallon of warm lubricant-coolant emulsion to pass through a double thickness of Whatman No. 30 filter paper, 7 centimeters in diameter, under suction. Acceptable range is 5-8 minutes, at a 10 pounds per square inch differential pressure (absolute). Higher values may indicate malfunction of the filter leading to excessive dirt build-up, or it may indicate low chelant salt and/or high tramp oil concentration.

15 5. *pH-Lubricant-coolant sample is diluted to 1 percent and tested with a pH meter. The pH is inherently maintained in the range of 9 to 10 by the periodic addition of alkaline chelant salt.*

## EXAMPLE 2

The procedure of Example 1 was followed for a number of successive mill passes. Both aluminum plate and coil were rolled over a period of 7 days. The hardness of the lubricant emulsion gradually increased to about 250 p.p.m., calculated as  $\text{CaCO}_3$ . At this time 15 gallons of aqueous 38 percent tetrasodium ethylenediaminetetraacetic acid ( $\text{Na}_4\text{EDTA}$ ) was added to bring the hardness level down to 170 p.p.m., calculated as  $\text{CaCO}_3$ . In six more 8-hour shifts of operation, the hardness built up to 200 p.p.m. of ( $\text{CaCO}_3$ ). At this time, 5 gallons of 38 percent  $\text{Na}_4\text{EDTA}$  were added and the hardness dropped to 180 p.p.m. (as  $\text{CaCO}_3$ ) when sampled and analyzed 24 hours later. This procedure was repeated again after four more 8-hour shifts of operation in which the hardness was adjusted below 200 p.p.m.

25 Approximately 1 p.p.m. hardness build-up per hour was calculated from the  $\text{Na}_4\text{EDTA}$  additions for the system when rolling aluminum alloys containing Mg. In each instance the effect of the  $\text{Na}_4\text{EDTA}$  addition was to lower and maintain hardness level within the range of 100-200 p.p.m.

30 During this period, four 55-gallon drums of soluble oil concentrate containing emulsifying agent were added. Water losses up to 5,000 gallons per 24 hours were made up by adding de-ionized water.

35 At another time an estimated 200 gallons of hydraulic oil (220 SUS viscosity at 100° F.) entered the system because of a leak.

40 It was necessary to back-wash the precoated filter six times during a period of about 32 hours. The emulsion remained stable and the oil globules were maintained at an average particle diameter size of about 2 microns with no particles larger than about 5 microns. Lubricating properties of the emulsion were completely satisfactory during this period, and filterability permitted continued reuse of the emulsion which otherwise would have been discarded. Surface quality of the rolled aluminum product was good to excellent during this time.

## EXAMPLE 3

The procedure of Example 1 was followed for a large number of successive mill passes. Some of each of aluminum plate and coil and magnesium plate and coil were rolled interchangeably on the same mill over a period of 15 months. The hardness of the lubricant emulsion gradually increased periodically to about 250 p.p.m., calculated as  $\text{CaCO}_3$ . Each time the hardness reached such a level of concentration, about 15 gallons of aqueous 38 percent tetrasodium salt of ethylenediaminetetraacetic acid was added to the emulsion to bring the hardness level down to about 150 to 100 p.p.m., expressed as  $\text{CaCO}_3$ . In each instance the hardness level was reduced so as to maintain hardness within the range of about 100-200 p.p.m., expressed as  $\text{CaCO}_3$ . Occasionally a 55-gallon

drum of soluble oil concentrate containing emulsifying agent was added to the emulsion to make up for base oil taken out by the filter and especially for accidental spillage or sewerage of the emulsion. Water losses due to evaporation and drag-out amounting to as much as 5,000 gallons per 24 hours were made up by adding needed amounts of de-ionized water.

Occasionally a relatively small quantity of hydraulic oil not exceeding about 200 gallons and having a viscosity at 100° F. of about 220 Saybolt seconds entered the system because of accidental leakage. Such oil was taken up during pumping and handling of the emulsion, disappeared and was no longer present as a free coalesced phase.

Throughout the period of use the emulsion was filtered using the filter and precoat described in Example 1. During periods of active use, the emulsion was filtered steadily during transfer from the dirty compartment 7 to the clean compartment 6. During such times the filter was back-washed and recoated about every 48 hours.

Throughout the 15 month period the emulsion remained stable and clean and readily filterable. The oil globules of the emulsion remained in stable form with an average globule diameter in the range of 1 to 2 microns with no globules larger than about 5 microns. In general, no coalesced or continuous phase of free oil (in excess of about 0.2 percent by weight) appeared except during accidental leakage into the system of unusually large quantities of hydraulic oil. The lubricating properties of the emulsion were completely satisfactory during this period and the surface quality of the rolled metal was good to excellent throughout the entire period.

#### EXAMPLE 4

Cold rolling of steel is carried out on a 5-stand tandem mill in which steel sheet is reduced in thickness from about 0.10 to 0.15 inch to about 0.015 to 0.05 inch. During rolling, the steel sheet and the rolls are lubricated by 1000 gallons per minute of an oil-in-water emulsion from a recirculating system containing 15,000 gallons of emulsion. About one gallon of neat oil is applied per 8,000 pounds of metal rolled. The base oil used in making up the emulsion is palm oil. The palm oil is emulsified with standard emulsifiers and constitutes about 3 percent by weight of the emulsion. At the start of using the emulsion, the emulsion pH is adjusted to about 8.5 and the hardness present in the emulsion is adjusted to about 100 p.p.m., expressed as  $\text{CaCO}_3$ , by the addition of the requisite amount of the trisodium salt of nitrilotriacetic acid.

During rolling, the emulsion flooding the rolls and cascading over the sheet metal is collected in an underlying sump, pumped to dirty storage, then filtered through a precoated mechanical filter employing a siliceous material for precoat and capable of removing solid particulate matter larger than 1 micron size. The filtered emulsion is collected in clean storage and is again promptly reused in the mill. Periodically, the emulsion being pumped to the filter is sampled, analyzed, and the requisite additions of the sodium salt of nitrilotriacetic acid are made to maintain the pH of the emulsion in the range of 8.5 to 9.5 and the hardness content of the emulsion in the range of 100 to 200 p.p.m., expressed as  $\text{CaCO}_3$ . Periodically, additions of water and of neat soluble oil are made to compensate for losses by evaporation and drag-out. Periodic tests show that the oil globule sizes in the emulsion remain stable at an average size of about 15 microns diameter with substantially no globules larger than 40 microns diameter.

After a period of 19 months, the emulsion remains stable and substantially free of continuous free oil phase, the oil globule sizes remain stable at about 15 microns diameter, the sheet steel is satisfactorily reduced in thickness in the rolls and the surface of the rolled metal is

smooth and bright and substantially free of surface imperfections.

#### EXAMPLE 5

Cold rolling of brass is carried out on each of a 2-high reversing breakdown mill, a 2-high rundown mill, and a 4-stand tandem finish mill. In typical operations, continuous cast 26 inch wide flat brass bars each weighing about 3,000 pounds are cold rolled from 3.25 inch thickness to 0.540 inch gauge flat plate on the breakdown mill. Nine passes and two intermediate anneals are required to accomplish the reduction in thickness. The rolls and workpieces are lubricated by a flow and spray application of 800 gallons per minute of a recirculating, filtered, lubricant-cooled oil-in-water emulsion from a system containing 16,000 gallons of emulsion. The emulsion has a neat soluble oil concentration of about 12 percent by weight, average oil globule diameters of about 1 to 2 microns, a hardness content of 100 to 200 p.p.m., expressed as  $\text{CaCO}_3$ , and a pH of about 7.8 to 8.5. Hardness and pH are maintained by periodic additions of the trisodium salt of nitrilotriacetic acid to the emulsion. Overhauling (scalping) removes any stain that develops on the rolled plate.

On the rundown mill brass strip is rolled from 0.500 to 0.102 inch thick without annealing. On the finish mill, strip is rolled from 0.102 inch thickness to 0.012 inch gauge with intermediate anneals as necessary. The workpieces and the rolls of each mill are cooled and lubricated with 650 gallons per minute of a recirculating, filtered lubricant-coolant oil-in-water emulsion from a common system holding 20,000 gallons of emulsion. The emulsion has a neat soluble oil concentration of about 7 percent, an average oil globule diameter in the range of about 5 microns, a hardness content maintained in the range of 25 to 75 p.p.m., expressed as  $\text{CaCO}_3$ , and a pH of about 7.3 to 7.8. The emulsion is made up from the soluble oil Prosol 66, supplied by Socony Mobil Vacuum Company, Prosol 66 soluble oil is low in sulfur compounds and is non-staining of copper and copper alloys. Hardness and pH are maintained by periodic additions to the system of the tetramonium salt of ethylenediaminetetraacetic acid. Routine losses of emulsion are made up adding new emulsion to the system.

After continuous operation of each mill and emulsion system for over 12 months, examination of each shows that rolling is carried out satisfactorily, the rolled brass products exhibit an excellent surface appearance, and the reused emulsions are clean and stable and filterable through a filter capable of removing solid particulate matter larger than about 1 micron size.

#### EXAMPLE 6

In a shop in which precision grinding is carried out, an oil-in-water emulsion containing 1 percent by weight of a soluble oil is supplied to each of 15 grinders at a rate of 20 gallons per minute and lubricates and cools the workpieces and the grinding wheels. At each grinder, the used emulsion flows onto a collecting plate having a central depression covered by a coarse screen (0.2 inch screen openings) and piping means draining the collecting plate to a common sump. Emulsion collected in the sump is pumped to a filter employing a microcel membrane which passes particulate no larger than 1 to 2 microns size. Filtered emulsion collects in a clean storage compartment until recirculated to the grinders. The emulsion has an average oil globule diameter in the range of about 1 to 2 microns, a hardness content maintained in the range of 100 to 200 p.p.m., expressed as  $\text{CaCO}_3$  and a pH of about 8.5 to 9.5. Hardness and pH are maintained by periodic additions of the disodium salt of N-2-hydroxyethyliminodiacetic acid. Emulsion losses are made up by the addition of fresh soluble oil and tap water and

enough disodium salt of N-2-hydroxyethyliminodiacetic acid to maintain the said hardness level. After 13 months of operation the emulsion system is clean and stable, the emulsion globule sizes have not substantially changed, and the emulsion remains readily filterable and reusable in the grinding operations. 5

In a manner similar to each of the foregoing, the sodium, potassium, ammonium, and amine salts of each of ethylenediaminetetraacetic acid, N-hydroxyethylmethylenediaminetriacetic acid, N - 2 - hydroxyethyliminodiacetic acid, diethylenetriaminepentaacetic acid, nitrilotriacetic acid and cyclohexanediaminetetraacetic acid are useful in controlling and maintaining oil-in-water lubricant-coolant emulsions employed in metal shaping operations including rolling, working, drawing, cutting, milling, scalping, drilling, machining and grinding of magnesium, aluminum, copper and ferrous metal.

The mode of operation of the chelating agents employed in the present invention is not clearly understood, but it appears that the polyvalent metal ion control obtained critically affects the hydrophile-lipophile balance obtaining in the lubricant-coolant emulsions whereby the emulsions are rendered surprisingly stable and globule diameters substantially do not change when the emulsions are managed according to the invention.

The emulsions managed and reused according to the invention, including fine filtering are further characterized by surprisingly low ion concentrations of metals such as aluminum, iron and silicon, the ion concentrations, respectively, remaining generally below about 1 to 30 p.p.m. Moreover, metal surfaces in continuous or repeated contact with the present treated emulsions seem to become passivated toward the emulsions so that there is little metal ion uptake.

Among the advantages of the invention is the bacterial control achieved without the necessity of adding a bactericide. The chelating agents employed tie up substantial proportions of metal ions in the emulsions which would otherwise react with metal surfaces to provide molecular hydrogen. Molecular hydrogen, which has a powerful catalytic effect on the growth of anaerobic bacteria, is largely avoided. Moreover, wherein fine filtration is carried out, initial bacterial growth is largely filtered out so that colonies are not readily established. Removal of metal fines by filtration also removes metal fines which would otherwise contribute to the electrochemical action which provides the undesired molecular hydrogen.

Another advantage of the stable emulsions and the method of the invention is the avoidance of the problems associated with (1) cleaning up a system after an emulsion breaks, and (2) starting up a system with a completely new emulsion or after a major addition to a used emulsion. New emulsions need to be used up to 2 weeks before they exhibit really good filterability. Even major additions, e.g., at least one-fourth of system capacity, 55 necessitate shorter filter cycles for some days.

The method and composition of the invention having been thus fully described, various modifications thereof will at once be apparent to those skilled in the art and the scope of the invention is to be considered limited only by the breadth of the claims hereafter appended. 60

I claim:

1. In a method of cooling and lubricating a metal during the shaping thereof wherein the work piece and the tool are contacted with a flowing lubricant-coolant oil-in-water emulsion and said emulsion is recycled and reused steadily, in said shaping, over a period of at least several months, the steps which comprise:

adjusting and maintaining (1) the hardness level of the aqueous phase of the emulsion below about 400 p.p.m., expressed as  $\text{CaCO}_3$ , and (2) the pH value of the emulsion within the range of about 5 to 11 by periodic additions to the emulsion of the requisite amounts of a chelant selected from the group con-

sisting of alkali metal salts, ammonium salts and amine salts of a polycarboxylic acid chelating agent whereby the emulsion is stabilized and is further characterized by ready filterability; and passing from about one-third to substantially all of said emulsion, after use and prior to reuse, through a mechanical filter; said metal being selected from the group consisting of aluminum, copper and ferrous metal.

10 2. The method as in claim 1 wherein the hardness is maintained in the range of about 25 to 400 p.p.m., expressed as  $\text{CaCO}_3$ .

15 3. The method as in claim 1 wherein the hardness is maintained in the range of about 100 to 200 p.p.m., expressed as  $\text{CaCO}_3$ .

15 4. The method as in claim 1 wherein the pH is maintained in the range of about 7 to 10.

20 5. The method as in claim 1 which includes the further steps of periodically sampling and analyzing the emulsion for hardness and pH, and adding chelant in the requisite amount to maintain each of the hardness level of the aqueous phase and the pH value within the said ranges.

25 6. The method as in claim 1 in which mechanical filtration is carried out to remove from the emulsion particles larger than a preselected size in the range of about 0.5 to 10 microns.

25 7. The method as in claim 1 wherein the chelant employed is a salt of an alkylene amino polyacetic acid.

30 8. The method as in claim 1 wherein the shaping method is rolling and the emulsion comprises (1) from about 2 to about 15 percent by weight of neat soluble oil, (2) spent chelant, the chelant being combined with polyvalent metal ions, (3) from about 25 to 400 p.p.m. of unchelated hardness, expressed as  $\text{CaCO}_3$ , and (4) the balance substantially water, and the further steps which comprise:

35 (a) contacting the rolls and the metal work piece with said emulsion as the work piece enters the rolls of the mill;

40 (b) passing said work piece between said rolls thereby to reduce the thickness of said work piece;

(c) collecting said emulsion after use on the work piece and the rolls;

(d) analyzing said emulsion for hardness;

45 (e) adding an alkali metal salt, ammonium salt, or amine salt of a polycarboxylic acid chelating agent to the emulsion in the requisite amount to adjust the hardness content of the aqueous phase of the emulsion to 25 to 400 p.p.m., expressed as  $\text{CaCO}_3$ , and the pH to a value in the range of about 7 to 10;

50 (f) passing at least  $\frac{1}{3}$  of said emulsion after use through a filter thereby to remove solid particles larger than a predetermined size in the range of about 0.5 to 10 microns;

55 (g) and recycling said filtered emulsion from the filter to the said rolls.

#### References Cited

#### UNITED STATES PATENTS

Re. 23,905	12/1954	Bersworth	260—518
2,631,978	3/1953	Bersworth	252—33.6
2,663,704	12/1953	Yehling	260—217
2,770,597	11/1956	Jezl	252—49.5 XR
2,780,598	2/1957	Cafcas	252—34.7 XR
2,794,000	5/1957	Ruedrich	252—49.5 XR
2,802,788	8/1957	Flaxman	252—105
2,959,547	11/1960	Brillhart	252—33.6
2,432,784	12/1947	Miller	252—49.3
3,301,783	1/1967	Dickson et al.	252—49.5 XR
2,264,103	11/1941	Tucker	210—23

(Other references on following page)

15

#### OTHER REFERENCES

Lubricating Engineering I, October 1951, pp. 223-227.  
 Lubricating Engineering II, July 1959, pp. 85-99.  
 Metal Industry, April 1958, pp. 271-273, Fishlock.  
 Chemistry of the Metal Chelate Compounds, Prentice-Hall Inc., Pub. 1953, Martell et al., pp. 487-495 and 511-512.

16

Theory of Emulsions, 5th Edition, 1954, The Blackiston Co. Inc., Pub. Clayton, pp. 34 and 192-206.

DANIEL E. WYMAN, *Primary Examiner.*

W. H. CANNON, *Assistant Examiner.*