

UNITED STATES PATENT OFFICE

2,420,328

LUBRICANT FOR PROCESSING METALS

Joseph Harrel Shipp, Wilmington, Del., and
Charles J. Pedersen, Penns Grove, N. J., assign-
ors to E. I. du Pont de Nemours & Company,
Wilmington, Del., a corporation of Delaware

No Drawing. Application May 26, 1945,
Serial No. 596,078

20 Claims. (Cl. 252—49.5)

1

This invention relates to new compositions of matter and particularly to aqueous emulsions especially adapted for lubricating metals during processing operations, such as cutting, drawing, drilling, tapping, milling, stamping and the like.

For many years there has been a problem of improving lubricants used in cutting and drawing metals and in various other metal processing steps. In many cutting operations, such as those performed on lathes, drill presses and milling machines, it is very difficult to keep a lubricant at the cutting point due to the continual flow of metal past this point under extreme pressures. The ideal lubricant would be one which could be applied to the cutting edge before cutting was begun, and which would cling tenaciously to that edge and facilitate the sliding of the metal surfaces by the cutting edge. Without proper lubrication at the cutting edge, there is a tendency for metal to build up on the cutting tool and this impairs cutting. Likewise, in other metal cutting operations where high pressures are involved, there is a tendency for metal to metal contact between cutting tool or die and metal being processed, unless a tenacious lubricant is used. As a result, there is a welding of the two metals which eventually causes scoring or tearing out of metal, giving a rough surface to the object being processed. This problem exists in cutting, drawing, stamping and other operations.

In the cutting of soft metals, the difficulty is accentuated due to the low resistance of the metals to deformation under pressure. Thus, in tapping holes in aluminum, there is a tendency to tear out the metal and give an over size hole unless a highly efficient lubricant is used. Due to this fact, it was difficult to get close fitting threads in aluminum. It has been customary to use under-size taps in tapping aluminum and other soft metals. This necessitates two sets of taps where one set of taps would be sufficient if a satisfactory lubricant were used. In tapping hard metals to give close clearance threads, there is also some tendency for some of the harder crystals of some alloy metals to be pulled out rather than cut through. This results in an unevenly cut surface. To minimize the tearing out of these crystals, it is often necessary to resort to laborious hand tapping to obtain close clearances.

It is an object of the present invention to provide new and useful emulsions. Another object is to provide novel emulsions particularly adapted for lubricating metals during metal processing operations. Still another object is to provide improved metal processing lubricants, and particularly lubricants which are stable and non-corrosive toward metals. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

2

The above and other objects may be accomplished in accordance with our invention which comprises providing an aqueous emulsion of a "Lorol" residue in which the emulsifying agent is a surface-active water-soluble non-acidic salt of an acid-ester of phosphoric acid. We have found that such emulsions are effective lubricants for metal processing operations, such as cutting, drawing, drilling, tapping, milling, stamping and the like. Such emulsion is particularly effective as a lubricant in tapping both hard and soft metals and in cutting, drilling and drawing of soft metals.

The term "Lorol" residue, as employed herein and in the claims, means the distillation residue of a hydrogenated fatty oil. The "Lorol" residue is obtained by the carboxyl hydrogenation of a natural fatty oil in the presence of a hydrogenation catalyst until the major proportion, at least 70%, of the carboxyl groups have been reduced, followed by separation of the hydrogenation catalyst and distillation of the reaction mixture to remove substantially all alcohols up through octadecyl alcohol.

Suitable methods of carrying out the hydrogenation are well known and are illustrated by those disclosed in Patent 2,023,383 to Schrauth et al. and Patent 2,094,127 to Lazier. Since the original esters, constituting the major proportion of the fatty oils, do not have the desired lubricating properties, the hydrogenation should be carried out so as to obtain substantially complete reduction of the carboxyl groups, that is, as far as is practicable.

After the hydrogenation, the mixture is filtered to remove the catalyst. The reaction mixture is then subjected to a distillation to distill off substantially all alcohols up through octadecyl alcohol. This distillation will preferably be carried out under reduced pressure. The residue left in the still is a "Lorol" residue. It is a product of indeterminate composition and appears to contain higher alcohols, esters of higher alcohols, ethers of higher alcohols, hydrocarbons, glycerine and esters of glycerine with the ethers of the higher alcohols predominating. A typical "Lorol" residue gave the following data on analysis:

Hydroxyl number	380
Saponification number	8.1
Iodine number	4.7
Molecular weight (av.)	380
Ash	Nil
Carbon	81.08
Hydrogen	14.24
Oxygen (by difference)	4.68

Frequently, it is desirable to subject this residue to a further hydrogenation and distillation so as to recover more of the valuable alcohols

and to reduce the proportion of esters in the residue.

The "Lorol" residue may be derived from any natural fatty oil, either animal or vegetable. We have obtained particularly satisfactory results with products derived from vegetable oils, such as coconut oil, palm oil, cotton seed oil and olive oil.

The "Lorol" residue by itself is an excellent lubricant for the processing of metals. However, it is a semi-solid material at room temperatures and cannot be circulated unless it is heated above its melting point. However, we have found that the "Lorol" residue can be readily emulsified in water and the resulting emulsion is a particularly effective lubricant for the processing of metals. Many of the common emulsifying agents will be effective to emulsify the "Lorol" residue in water. However, most of such emulsifying agents are unsuitable for the reason that the resulting emulsions will cause corrosion or rusting or discoloration of the metals, and particularly such metals as iron, aluminum and copper.

We have found that the water-soluble non-acidic salts of the acid-esters of phosphoric acid which are surface-active, that is, which have emulsifying properties, are particularly effective for emulsifying "Lorol" residues in water to produce non-corrosive, non-rusting and non-discoloring emulsions. An "acid-ester" of phosphoric acid is one in which from 1 to 2 of the hydrogens of phosphoric acid has been replaced by an esterifying group and which contains from 1 to 2 un-replaced hydrogen atoms. The esterifying group may be any organic group which imparts substantial surface activity to the compound. Suitable esterifying groups are long-chain alkyl, alkyl substituted aryl, aralkyl and the like. Aryl groups may also be present, particularly when mixed with long-chain alkyl groups. By "long-chain alkyl," we mean open-chain aliphatic hydrocarbon groups of 8 or more carbon atoms. Preferably, the long-chain alkyl groups will contain from 8 to 20 carbon atoms. Representative long-chain alkyl groups are octyl, decyl, dodecyl, tetradecyl, hexadecyl and cetyl. Suitable alkyl substituted aryl groups are isopropyl-naphthyl, laurylphenyl and the like. Preferably, the acid-esters will be mixtures of mono and di-esters containing about 1.5 esterifying groups for each phosphate radical. The esterifying groups may be a mixture of 2 or more different groups, at least one of which must impart appreciable surface activity to the compound. Best results have been obtained with acid-esters containing about 1.5 long-chain alkyl groups of 8 to 18 carbon atoms per phosphate radical.

The salts of the acid-esters are those in which the ester has been completely neutralized by a basic salt-forming substance which forms, with the ester, a surface-active water-soluble salt. Suitable basic salt-forming substances include primary, secondary and tertiary amines, particularly mono-, di- and trialkylamines and alkylolamines. Preferably, the basic salt-forming substance will be a short-chain aliphatic amine and particularly an alkylolamine, such as triethanolamine. The basic salt-forming substance may be ammonia or an alkali metal, but these are not preferred since the resulting salts are less effective and are less desirable because of a tendency to produce corrosive products. The basic salt-forming substance may be used in excess provided that it does not produce a pH in excess of 10 in the final product as a 10% solution. With

the less basic amines and the alkylolamines, an excess of up to 100% of that required to neutralize the ester may be used. With strong bases care must be taken to avoid such excess as will cause corrosion of the metals.

The concentration of the "Lorol" residue in the emulsion may be widely varied in accordance with the use to which it is to be put. Where the emulsion is to be employed as a coolant, as well as a lubricant, and applied by a circulating pump or the like, the "Lorol" residue should be present in a concentration of from about 1% to about 5% and preferably from about 2% to about 4%. Where the lubricant is to be applied to the work and tool by brushing or the like, the "Lorol" residue will be present in the emulsion in a concentration of approximately 10%. Ordinarily, the emulsion will be marketed as a concentrate to be further diluted for use. In such concentrate, the "Lorol" residue will usually be present in a concentration of from about 40% to about 55%. The concentrated emulsion may contain higher concentrations of "Lorol" residue up to about 70%, but such concentrations will usually be undesirable as they are quite viscous and are difficult to stir into water to obtain the desired diluted emulsion for use.

The proportion of the emulsifying agent in the emulsion may be widely varied and will be largely dependent upon the effectiveness thereof as an emulsifying agent. For practical purposes, sufficient emulsifying agent should be used to provide a stable emulsion. A substantial increase of the emulsifying agent over that required to provide a stable emulsion will usually be undesirable because it increases the tendency of the emulsion to foam during use. We have employed satisfactorily proportions of emulsifying agent ranging from as little as 2% to as much as 50% based on the "Lorol" residue. With the preferred emulsifying agents, we have obtained very satisfactory results employing from about 3% to about 10% of the emulsifying agent based on the "Lorol" residue.

Representative concentrated preparations, which have been employed satisfactorily in commercial applications, had the following compositions:

	#1	#2
	Parts	Parts
"Lorol" Residue.....	40	40
Pine Oil.....	12	12
Alkyl phosphate ¹	0.75	1.5
Triethanolamine.....	0.75	1.5
Water.....	46.50	45.00

¹ This is a mixture of esters of phosphoric acid containing about 1.5 alkyl groups per phosphoric acid radical, the alkyl groups being derived from a mixture of primary straight-chain aliphatic alcohols of 8 to 14 carbon atoms.

In order to more clearly illustrate our invention, the preferred modes of carrying the same into effect and advantageous results to be obtained thereby, the following examples are given:

Example 1

One and one-half lbs. of a mixture of mono and di-lauryl phosphates, containing about 1.5 lauryl groups per phosphate radical, was added to 45 lbs. of water. One and one-half lbs. of triethanolamine was added and the solution heated to 60° C. Fifty-two lbs. of the residue, obtained by hydrogenating coconut oil as described in U. S. Patents 2,094,127 and 2,023,383, distilling off the alcohols up through octadecyl alcohol, re-

5

hydrogenating to further convert esters into alcohols, and distilling off these alcohols, was heated to 60° C., at which temperature it was molten. This molten residue was then poured slowly into the triethanolamine-lauryl-phosphate solution with vigorous stirring. The residue was emulsified to give a particle size of 2 to 3 microns. A thick creamy emulsion was formed which could be readily dispersed in hot water.

Example 2

One and one-half grams of the mixed mono and di-octyl esters of phosphoric acid, containing about 1.5 octyl groups per phosphate radical, and one and one-half grams dicyclohexylamine were dissolved in 45 lbs. water and the solution heated to 60° C. To this solution was added, with stirring, 52 lbs. of the distillation residue left in the still after distilling off the alcohols up through octadecyl alcohol from a hydrogenated palm oil. A thick creamy emulsion was obtained.

Example 3

The emulsion, described under Example 1, was diluted by adding 10 parts of water to 1 part of the emulsion. This diluted emulsion was then used as a coolant and lubricant for drilling a 1 7/8 inch hole in a 2 3/8 inch steel rod 10 feet long. By the use of this coolant and lubricant, it was possible to drill at a much more rapid rate than had been possible with mineral oil lubricants. Furthermore, a smoother hole was drilled and the tool life was increased. Another advantage of the aqueous system in this drilling operation was that the chips were removed more efficiently, so that drilling could be carried on continuously. In this operation, the coolant-lubricant was pumped through holes through the drill so that it flowed back over the drill, carrying the chips with it.

Example 4

The emulsion, described in Example 2 above, was used to lubricate a tap during the tapping of a 5/8 inch hole in an aluminum casting. The emulsion was brushed onto the tap during the tapping operation. After the tap was removed, the hole was found to be properly threaded when tested with a "go-no go" gauge. This gauge is so designed that, when a hole is properly threaded, the "go" end of the gauge will screw into the hole very snugly and the "no go" end will not screw into the hole at all. With other lubricants, it had been found that the "go" end of the gauge fitted very loosely in the threaded hole and even the "no go" end would screw into the hole. With ordinary lubricants, it was possible to obtain reasonably good fits only by using under-size taps. No corrosion or staining of the aluminum occurred with the emulsion.

Example 5

The emulsion, described in Example 1, was used as a lubricant in the tapping of 1 1/4 inch holes in a chrome-manganese steel plate. An exceedingly close fitting thread was specified. Using previously available lubricants, it was possible to obtain a class three thread only when resorting to hand tapping. This required eight hours of time for the tapping of a given number of holes. When the emulsion, described in Example 1, was used and applied by brushing onto the taps, it was found that a much cleaner cut and a much better class of thread was obtained. It was possible to tap these holes by machine with this lubricant and obtain a very high quality thread

6

within specifications. By the machine tapping operations, it was possible to cut down the time required from eight hours to two hours for one unit of this work. No corrosion of the metal was noted in this operation.

Example 6

Forty lbs. of residue, left in the still after distilling a hydrogenated coconut oil, hydrogenated according to U. S. Patent 2,023,383, was mixed with 10 lbs. of pine oil and then emulsified with 50 lbs. of a 5% aqueous solution of the triethanolamine salt of a mixed dodecyl and decyl phosphate by stirring with a high speed stirrer. The phosphate was prepared from a mixture of equal parts of dodecyl and decyl alcohols and contained about 1.5 alkyl groups per phosphate radical. The pine oil was added to inhibit foaming of the emulsion during use. The resulting emulsion was diluted with 10 parts of water for 1 part of emulsion, and the diluted emulsion used as a coolant and lubricant in drawing dynamite blasting caps from aluminum stampings. These dynamite caps were extremely thin walled and yet there was no indication of tearing or scoring when the above lubricant was used. With ordinary lubricants, it had been noted that a large number of caps had torn edges and scored surfaces. It was also noted that, with the lubricant prepared according to this invention, the life of the dies was greatly increased. Similar blasting caps were drawn from gilding metal, which is a high copper content alloy, and an equal improvement was noted over the use of other lubricants. There was no corrosion of the bright surface of either the aluminum or the gilding metal, even when the lubricant was left in contact with the metal for several hours.

Example 7

A one inch rod of cold rolled steel was threaded, using the concentrated emulsion described in Example 6 as lubricant. The lubricant was brushed onto the metal and onto the die during hand threading. The surfaces of the cut threads were examined under a magnification of ten times. It was noted that an extremely smooth cut was obtained, when compared with a similar rod threaded with the same die, but using a sulfurized cutting oil as lubricant. Likewise, a one inch hole was tapped in a high carbon steel, using the emulsion of Example 6 as lubricant. After tapping, the metal was cut through the hole and the threads viewed under ten-power magnification. Again it was observed that a very smooth cut had been obtained.

Example 8

A sample of olive oil was hydrogenated by the procedure described in U. S. Patent 2,094,127. The hydrogenation mass was filtered to remove the catalyst and then subjected to distillation under diminished pressure to distill off the alcohols formed by hydrogenation. When substantially all of the alcohols up through octadecyl alcohol had been removed, the residue was again hydrogenated and a second distillation carried out. The residue, from this distillation, was then emulsified by heating it to 60° C. and adding it to a solution containing 1 1/2% of the triethanolamine salt of an alkyl phosphate containing about 1.5 alkyl groups per phosphoric acid residue, the alkyl groups being a mixture of octyl and cetyl in the ratio of 6 cetyl to 4 octyl groups. Fifty grams of the hydrogenation residue were emulsified in 50 grams of the aqueous solution. The resulting

7

emulsion was diluted with 4 parts of water and the dilute emulsion was used as a lubricant in the chasing of threads on a stainless steel valve stem $\frac{3}{4}$ " in diameter. A very smooth surface cut was obtained and the threads were free of the ridge cracks and checking noted with most lubricants.

Example 9

Twenty pounds of pine oil were added to 40 lbs. of the residue from the distillation of hydrogenated cotton seed oil. The pine oil and residue were heated to 60° C. and poured with violent stirring into 50 lbs. of water containing 4% of the salt of 2-amino 2-methyl propanol-1 and decyl phosphoric acid in which $1\frac{1}{2}$ alkyl groups are present for each phosphoric acid unit. This emulsion was diluted with 20 parts of water and used as a coolant and lubricant for tapping holes in aluminum alloy crank cases. The purpose of the pine oil in this example was to prevent excessive foaming of the emulsion. With this lubricant, very clean cut threads were obtained using standard size taps and a close fit was also obtained as shown by the "go-no go" gauge. A similar emulsion, except that the pine oil was omitted, foamed to an objectionable degree but the foaming was overcome by the addition of pine oil.

Example 10

Seven and one-half pounds of a mixture of mono and di-lauryl phosphates, containing about 1.5 lauryl groups per phosphate radical, was added to 27 pounds of water. Seven and one-half pounds of triethanolamine was added and the solution heated to 60° C. Eighteen pounds of "Tetralin" was added to forty pounds of a "Lorol" residue obtained from coconut oil and this mixture heated to 60° C. The "Lorol" residue-"Tetralin" solution was then added to the aqueous solution with vigorous stirring. A creamy emulsion was obtained which could be readily diluted with water. One pound of this emulsion was diluted with fifteen pounds of water and placed in a circulating system of a pipe threading machine. This machine was used for threading various size iron pipes. Microscopic examination of the cut surfaces of the threads showed a much smoother cut than had previously been obtained with a mineral oil lubricant. The tool life of the dies was also increased over that observed with mineral oil lubricant.

Example 11

This example is given for comparative purposes to further illustrate the advantages of the "Lorol" residue compositions of our invention. Tapping compounds were made up as follows:

	Per cent
1	
A mixture of alkyl phosphates ¹ -----	35.25
Triethanolamine -----	14.75
Water -----	50
2	
A mixture of alkyl phosphates ¹ -----	28.5
Triethanolamine -----	12.0
Lard oil -----	40.5
Water -----	19
3	
A mixture of alkyl phosphates ¹ -----	17.5
Triethanolamine -----	7.5
Mineral oil -----	25
Water -----	50

8

4

Octadecyl phosphate -----	50
Mineral oil -----	50

¹ A mixture of esters of phosphoric acid containing about 1.5 alkyl groups per phosphoric acid radical, the alkyl groups being derived from a mixture of primary straight-chain aliphatic alcohols of 8 to 14 carbon atoms.

The emulsions were made up to approximately the same consistency as that of Example 4 and used to lubricate a new tap in the tapping of aluminum. When the tapped holes were tested for a class 3 fit with a "go-no go" gauge, the above compositions were found to be unsatisfactory because the holes were oversize as shown by the fact that both ends of the gauge would screw into the holes. Also, when the holes and the taps were carefully cleaned and the taps were screwed back into the holes, the holes, obtained with the above lubricants, gave loose fits; whereas, under the same conditions, the holes, obtained with the compositions of our invention, gave very snug fits.

It will be understood that the foregoing examples are given for illustrative purposes solely and that our invention is not to be limited to the specific embodiments disclosed therein, but that many variations and modifications can be made without departing from the spirit or scope of our invention. For example, "Lorol" residues may be prepared from other vegetable oils and animal oils. Also, other salts of other acid-esters of phosphoric acid, which are emulsifying agents, may be substituted for those specifically mentioned.

By the use of the lubricants of our invention, there results a smoothly cut surface with very little scoring. They have been employed satisfactorily in the processing of such metals as aluminum, various steels, magnesium, copper and brass. This is readily demonstrated in tapping, threading, drawing, drilling, milling and turning operations. These beneficial effects are particularly apparent when these operations are carried out on soft metals, such as copper, zinc, aluminum and magnesium. Thus, in the drawing of extremely thinned walled dynamite blasting caps, there is usually a considerable tearing of the thin metal unless a lubricant of our invention is employed. Even when the metal is not torn, the surface may be scored to such an extent that the blasting cap is untrustworthy. By the use of the lubricants of our invention, it has been possible to greatly decrease the number of rejected blasting caps in such operations. Likewise, in the tapping of small holes in hard steel gun parts, it has been possible to greatly decrease the number of taps broken with other commonly employed lubricants.

The "Lorol" residues, employed in our emulsions, have usually been considered as waste materials. By our invention, we have been able to find a valuable use for such waste materials and, at the same time, to provide new and improved non-corrosive lubricants for the processing of metals.

We claim:

1. An aqueous emulsion of a distillation residue derived from a hydrogenated natural fatty oil by distilling off fractions up through octadecyl alcohol, in which the emulsifying agent is a surface-active water-soluble non-acidic salt of a long-chain alkyl acid-ester of phosphoric acid, the distillation residue being present in a concentration of from about 1% to about 70% and

11

distilling off fractions up through octadecyl alcohol, in which the emulsifying agent is a surface-active water-soluble mixture of non-acidic alkylamine salts of long-chain alkyl esters of phosphoric acid containing about 1.5 alkyl groups per phosphate radical, the distillation residue being present in a concentration of from about 1% to about 70% and the emulsifying agent being present in a minor proportion sufficient to form a substantially stable emulsion.

16. An aqueous emulsion of a distillation residue derived from a hydrogenated vegetable oil by distilling off fractions up through octadecyl alcohol, in which the emulsifying agent is a surface-active water-soluble mixture of non-acidic triethanolamine salts of long-chain alkyl esters of phosphoric acid containing about 1.5 alkyl groups per phosphate radical, the distillation residue being present in a concentration of from about 1% to about 70% and the emulsifying agent being present in a minor proportion sufficient to form a substantially stable emulsion.

17. An aqueous emulsion of a distillation residue derived from hydrogenated cocoanut oil by distilling off fractions up through octadecyl alcohol, in which the emulsifying agent is a surface-active water-soluble mixture of non-acidic alkylamine salts of long-chain alkyl esters of phosphoric acid containing about 1.5 alkyl groups per phosphate radical, the distillation residue being present in a concentration of from about 1% to about 70% and the emulsifying agent being present in a minor proportion sufficient to form a substantially stable emulsion.

18. An aqueous emulsion of a distillation residue derived from hydrogenated cocoanut oil by distilling off fractions up through octadecyl alcohol, in which the emulsifying agent is a surface-active water-soluble mixture of non-acidic triethanolamine salts of long-chain alkyl esters of phosphoric acid containing about 1.5 alkyl groups per phosphate radical, the distillation residue being present in a concentration of from about 1% to about 70% and the emulsifying agent being present in a minor proportion sufficient to form a substantially stable emulsion.

12

idue being present in a concentration of from about 1% to about 70% and the emulsifying agent being present in a minor proportion sufficient to form a substantially stable emulsion.

19. An aqueous emulsion of a distillation residue derived from hydrogenated palm oil by distilling off fractions up through octadecyl alcohol, in which the emulsifying agent is a surface-active water-soluble mixture of non-acidic triethanolamine salts of long-chain alkyl esters of phosphoric acid containing about 1.5 alkyl groups per phosphate radical, the distillation residue being present in a concentration of from about 1% to about 70% and the emulsifying agent being present in a minor proportion sufficient to form a substantially stable emulsion.

20. An aqueous emulsion of a distillation residue derived from hydrogenated cotton seed oil by distilling off fractions up through octadecyl alcohol, in which the emulsifying agent is a surface-active water-soluble mixture of non-acidic triethanolamine salts of long-chain alkyl esters of phosphoric acid containing about 1.5 alkyl groups per phosphate radical, the distillation residue being present in a concentration of from about 1% to about 70% and the emulsifying agent being present in a minor proportion sufficient to form a substantially stable emulsion.

JOSEPH HARREL SHIPP.
CHARLES J. PEDERSEN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,617,077	Nil	Feb. 8, 1927
1,717,939	Rolsen	June 18, 1929
2,023,383	Schrauth	Dec. 3, 1935
2,291,066	Waugh	July 28, 1942

Certificate of Correction

Patent No. 2,420,328.

May 13, 1947.

JOSEPH HARREL SHIPP ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 2, line 49, in the table, for the numeral "380" read 58; column 12, line 9, claim 19, for "wtaer" read *water*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 1st day of July, A. D. 1947.

[SEAL]

LESLIE FRAZER,
First Assistant Commissioner of Patents.