ABSTRACT OF THE DISCLOSURE

Water-soluble amine salts of styrene-maleic anhydride copolymer resins and half-esters thereof are employed in aqueous solutions as coolants and lubricants for metal working and operations. Metal working lubricant compositions are also formulated which comprise these amine salts along with extreme pressure agents such as amine salts of fatty acids and organic phosphate esters. Other additives may also be employed in the lubricating compositions of this invention.

This application is a continuation-in-part of copending application Ser. No. 712,965, filed Mar. 14, 1968, now abandoned.

WATER BASED LUBRICANTS

Howard D. Gower, Munster, Ind., and Bob G. Gower, Park Forest, and David W. Young, Homewood, Ill., assignors to Atlantic Richfield Company, New York, N.Y.


U.S. Cl. 252—34.7

26 Claims

2 well balanced, efficient cutting fluid. For, whereas one may exhibit generally good lubricating and cooling qualities, it may have an objectionable odor, be irritating to the nose and throat of the operator or cause foaming; which obscures the operator's view of the material being worked, another may have an agreeable odor, or none at all, and be non-irritating and safe for the operator, yet fail to produce a good finished surface on the workpiece, the finish perhaps being replete with microscopic ridges, grooves and surface cracks.

It is an object of this invention to provide an aqueous coolant for metal working which is improved with respect to bacterially-promoted or chemically-caused odor, germ-forming tendency, irritation of the skin, clarity and ash content. It is a further object of this invention to provide novel emulsifying agents for use in aqueous metal working lubricating compositions containing synthetic lubricants.

Now in accordance with the present invention is has been found that cooling, tapping, and other machining operations of a high degree of efficiency are obtained when conducted in the presence of aqueous solutions of water-soluble amine salts of styrene-maleic anhydride copolymers. In addition it has been found that these water-soluble amine salts are particularly effective as emulsifiers in aqueous lubricating compositions containing extreme pressure agents. The amine salts of this invention have been found to possess long term stability and good shelf life in aqueous lubricating compositions.

The amine salts of this invention can be formed by reacting sufficient of a suitable amine with either the styrene-maleic anhydride resin or its partial ester to react with free carboxyl groups present in the resin or its partial ester. The amount of amine reacted is sufficient to make the salt water-soluble and is often reacted with at least about 50% or even at least about 70% of the total carboxyl groups of the resin. The styrene-maleic anhydride resin is a copolymer of about 1 to 5, preferably about 1 to 3 moles of styrene per mole of maleic anhydride and has a molecular weight of about 700 to 80,000, preferably about 700 to 3,000. The partial esters which can be employed are often up to about 100% half-esters of the styrene-maleic anhydride copolymer, that is the copolymer has up to about 50% of the total number of carboxyl groups esterified, and are preferably about 25 to 60% half-esters. The esterifying alcohols with which the copolymer is reacted to form the partial esters include the water-soluble alcohols and capped glycols corresponding to the general formula:

$$R-(-O-R')_{x}-OH$$

wherein R and R' are aliphatic hydrocarbon radicals, preferably saturated, of about 2 to 6 carbon atoms, and x=0 to about 10 or 12. The total number of carbon atoms in R and a single R' is often less than about 7. Uncapped glycols having molecular weights of about 200-20,000 can also be employed, however, if uncapped glycols are used it is preferable that the styrene-maleic anhydride polymer first be "pre-esterified" to reduce its functionality and thus preclude the formation of an insoluble ester. That is, the resin can be esterified with an alcohol or capped glycol to form, for example, and at least about 50% half-ester, prior to esterifying with the uncapped glycol to form the 90-100% half-ester, for example. Suitable alcohols and
glycols for use in esterifying the styrene-maleic anhydride copolymer are, for example, n-propyl alcohol, ethyl alcohol, isopropyl alcohol, t-butyl alcohol, isomyl alcohol, capped polypropylene glycols, e.g., polyethylene glycol monobutyl ether, and capped polypropylene glycols, etc.  

Preparation of the styrene-maleic anhydride copolymer can be by known methods. A preferred method is by solution polymerization where the monomers are polymerized in a suitable solvent employing as a polymerization catalyst a free-radical catalyst, such as a peroxide, preferably benzoyl peroxide, dicumyl peroxide or an alkyl peroxy dicarbonate, at a temperature of about 75 to 300°C. or more. Suitable solvents include the aromatic hydrocarbon solvents, such as cumene, p-cumene, xylene, toluene, etc. Other suitable solvents are the ketones, such as methyl ethylketone. The preferred manner of carrying out the polymerization is by what is known as incremental feed addition. By this method the monomers and catalyst are first dissolved in a portion of the solvent in which the polymerization is to be conducted and the resulting solution fed in increments into a reactor containing solvent heated to reaction temperature, usually the reflux temperature of the mixture. 

When an aromatic solvent is employed as the solvent for the polymerization, the formation of the copolymer causes a heterogeneous system, the polymer layer being the heavy phase and readily recoverable by merely decanting the upper aromatic solvent layer and drying. On the other hand, when a ketone is the solvent, the formed copolymer is usually soluble in the solvent media so that recovery of the product necessitates a solvent-stripping operation. 

The water-soluble, salt-forming amines having boiling points above about 200°C. C. can be employed in the present invention to form the amine salts of the styrene-maleic anhydride copolymer or its partial ester. Preferred amines are tertiary amines such as, for example, trimethylamine, trifurfurylamine, and hydroxyl lower alkyl amines such as, for example, diethanolamines and triethanolamines. Glycol amines or capped glycol amines of molecular weights up to about 5,000 are also suitable. The ethanolamines are.

From about 10 to 70, preferably about 30 to 55 weight percent of the amine, about 10 to 85, preferably about 10 to 50 weight percent water; and about 1 to 40, preferably about 1 to 10 weight percent styrene-maleic anhydride copolymer resin or partially-esterified copolymer are present in the composition of this invention based on the weight of these three components. A preferred method of reacting the copolymer is to first dissolve the amine in the water and then add the copolymer while keeping the temperature below about 140°F. to minimize evaporation. Sufficient agitation may be employed to insure complete formation. 

The aqueous compositions of this invention comprising the water-soluble amine salt of styrene-maleic anhydride copolymer resins or partial esters may be employed alone as effective lubricating compositions. Alternatively, the composition of this invention may also be employed in aqueous solutions containing minor, effective amounts of water-soluble extreme pressure lubricating agents such as water-soluble amine salts of organic phosphate ester acids or of fatty acids of 12 to 20 carbon atoms, for example, triethanolamine oleate, diethanolamine oleate, and similar salts of the various water-soluble amines used to form the water-soluble salts of styrene-maleic anhydride polymers of the present invention. Recipients are generally effective in the composition of the present invention when employed in amounts of from about 2-15 weight percent, preferably about 4-10 weight percent. Where the same amine is employed to form the styrene-maleic anhydride salt as is used to form the salt of the fatty acid, the fatty acid may be added to the styrene-maleic anhydride resin or partial ester to the aqueous solution containing an amount of the amine in excess of that needed to form the styrene-maleic anhydride salt.

3,645,897

The organic phosphate ester acids which may be employed as E.P. agents in the present invention can be, for instance, primary, secondary, or tertiary esters of phosphoric acid and a hydroxylic monomer which can be exemplified by the C$_5$-C$_9$ alkanoils, phenols, including the alkyomonophenols, and monoalky-, monoary- and monoarylalkylethers of polylaketylene glycols. These phosphate compounds include those corresponding to the following general formula:

$$\text{O} - \text{P} - (\text{O}(-\text{CH}_2\text{CH}_2\text{O})_n\text{R}_n) - \text{O}$$

wherein R is a hydrocarbon radical having about 1 to 30, preferably 8 to 18 carbon atoms, x equals 2 to 10, preferably 2, y is 0 to 20, preferably 2 to 6, and n is 1 to 2. The R groups can be alkyl, aryl or mixed alkaryl radicals. These phosphate esters of this invention may be oil or water-soluble, depending to a degree on the value of y, although the size of R and x may also be factors in determining solubility. Generally oil-solubility tends to increase with larger values of R and x while water solubits tends to increase with larger values of y. If about y=8 or 10 the esters tend to be water-soluble while below y=5 they can generally be oil-soluble. In any event, where the esters are water-insoluble, salt-forming amine, for example, triethanol-amine, can be included in the composition to react with and solubilize the ester. At least about one part by weight of amine per part of phosphate ester can often be required to solubilize the ester in the water.

Phosphate esters useful as the extreme pressure lubricant component in the present invention include, for example, trioctyl phosphate, oxo-tridecyl phosphate, mixtures of mono- and dialkyl phosphate, lauryl polyethylene-oxide phosphate esters, nonylphenylpolyethyleneoxide phosphate esters and the like. Methods of preparation of the phosphate esters suitable for use in the composition of the present invention appear in abundance in the prior art. U.S. Pat. 3,033,889 to Chiddix et al. (herein incorporated by reference), for example, discloses the preparation of phosphate esters of branched chain (Oxo) alcohols suitable as to the phosphate lubricant in the present invention. Similarly, the preparation of suitable alkyl, aryl and mixed aryl-alkyl polyethyleneoxide phosphate esters is described in U.S. Pat. Nos. 3,004,056 to Nunn et al. and 3,004,057 to Nunn, both patents being herein incorporated by reference.

In addition to the amine salt of the copolymer, the E.P. agent, and the water, the composition of this invention may also contain various additives such as, for example, about 1 to 10 weight percent of an anti-foaming agent such as hexadecyl alcohol, or other monohydric alcohols of from about 6 to 20 carbon atoms; about 2-10 weight percent, preferably about 3-9 weight percent, boric acid or other suitable boron compound, such as borax, which forms boric acid on hydration, or a mixture of such compounds with low molecular weight amines such as methyl ethyl amine or tributyl amine and sodium nitrite which can provide protection against rust. Water-soluble glycols, such as hexylene glycols and polyethylene glycols of up to about 5,000 molecular weight, or capped glycols and polyglycols, such as diethylene glycol monoethyl ether, have been found to prevent film formation and tackiness on the machinery or product and improve settling of fine solids in the water and non-ionic surfactants may be employed in amounts up to about 30, preferably about 10 to 25, weight percent. Small amounts of water-soluble silicones can be added as anti-foaming agents and sodium nitrite may also be added as a corrosion inhibitor. It is preferred that the lubricant composition have a viscosity of below about 100 poise at 25°C.

In use the lubricating composition of this invention may be diluted with water, for instance, to a concentration of 1 part by weight of the cutting oil composition to about 5 to 100, preferably 1 to 50, parts by weight of water.
In accordance with the present invention, lubricating compositions were formulated as follows:

**EXAMPLE I**

<table>
<thead>
<tr>
<th>Composition (wt. percent)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene-maleic anhydride half-ester</td>
<td>15</td>
<td>10</td>
<td>28.6</td>
<td>10.2</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>29</td>
<td>20</td>
<td>11.5</td>
<td>13.3</td>
</tr>
<tr>
<td>Water</td>
<td>65</td>
<td>56</td>
<td>62</td>
<td>34</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>5</td>
<td>5</td>
<td>6.4</td>
<td>6.4</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>5</td>
<td>5</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Hexadecyl alcohol</td>
<td>5</td>
<td>5</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>8</td>
<td>8</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>88</td>
<td>88</td>
<td>88.0</td>
<td>88.0</td>
</tr>
<tr>
<td>Cetyl alcohol</td>
<td>12</td>
<td>12</td>
<td>12.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Sodium nitrite</td>
<td>4</td>
<td>4</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Organic phosphate ester</td>
<td>3</td>
<td>3</td>
<td>3.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

1 40% ethylene glycol monomethyl ether half-ester of styrene-maleic anhydride copolymer having a molecular weight of about 1,000 and a mol ratio of styrene to maleic anhydride of 1:1.
2 Reaction product of styrene-maleic anhydride copolymer having a molecular weight of about 1,000 and an oleic acid.
3 Mixture of approximately equal amounts of primary and secondary phosphate esters of the ethylene end of oleyl alcohol, the other containing an average of 6 oxyethylene groups.

Surface grinder tests were performed on hard alloy cast iron using a carborundum wheel. Results are compared in Table I using Composition D of Example I at a dilution of 1 part of cutting oil lubricant to 50 parts of water and a commercial water-soluble metal cutting fluid at the same dilution.

**TABLE I**

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Grind ratio &lt;sup&gt;1&lt;/sup&gt;</th>
<th>Break in (run 60 additional passed)</th>
<th>Run 90 passed</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>18.55</td>
<td>12.2</td>
<td>15.0</td>
</tr>
<tr>
<td>Commercial water based cutting fluid</td>
<td>17.06</td>
<td>12.2</td>
<td>15.0</td>
</tr>
</tbody>
</table>

1 Grind ratio = metal removed/weight wear tests were conducted at a grinding wheel speed of 2,300 r.p.m., moving the specimen back and forth for the indicated number of passes over the wheel.

**EXAMPLE II**

Other fluids were prepared according to the following formulations:

<table>
<thead>
<tr>
<th>Component</th>
<th>Fluid A</th>
<th>Fluid B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene-maleic anhydride copolymer half-ester</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Hexylene glycol</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Extreme pressure phosphate additive</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Hexadecyl alcohol</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Water</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>Silicone anti-foam agent</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

1 Reaction product of styrene-maleic anhydride copolymer having a mole ratio of styrene to maleic anhydride of 1:1, and molecular weight of about 1,000 and methoxy polyethylene glycol of molecular weight of about 360.
2 Organic phosphate ester sold of Example I.

Note.—Fluids A and B passed the skin irritation tests.

Surface ground tests, as in Example I, Table I, and tapping tests were performed with composition B and commercial water-soluble metal cutting fluids at the same dilution. The results are reported in Table II.

**TABLE II**

<table>
<thead>
<tr>
<th>Tapping torque test &lt;sup&gt;1&lt;/sup&gt;</th>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel A</td>
<td>Steel B</td>
</tr>
</tbody>
</table>

1.1% | 0.6% Extremes

**Sample: 10% H₂O dilution**

<table>
<thead>
<tr>
<th>Torque, percent reference (in. lb., percent reference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compositions X</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>321/172</td>
</tr>
<tr>
<td>326/173</td>
</tr>
<tr>
<td>418/200</td>
</tr>
<tr>
<td>358/170</td>
</tr>
</tbody>
</table>

1 Composition X was used as a reference by dividing the torque for each sample by reference torque to give percent reference.

A.I.S.I. No. 1117.
A.I.S.I. No. 820.
A.I.S.I. No. 1018.
A.I.S.I. No. 1018.

Compositions X, Y, and Z are commercial fluids.

Grind ratio = metal removed/weight wear tests were conducted at a grinding wheel speed of 2,300 r.p.m., moving the specimen back and forth for the indicated number of passes over the wheel. The amount of metal removed and the specimen thickness were determined for each set of tests and the grinding ratio for each set computed from the test conditions. Other test conditions followed this table.

In the grinding tests the following materials and procedures were used.

**Grinding wheel**

Norton 80 mesh aluminum oxide type wheel, 8" x 3/4" x 1/4" hole. Step dressed to provide a working width of approximately 0.275" with the remainder undercuts some 0.040" to 0.060" to provide a reference surface for wear measurement.

**Work material**

AISI E 2150 (modified) steel identified as PS 216 from Peterson Steel, Inc., Melrose Park, Ill. The modification from the basic specification was approximately a 1% increase in manganese to raise the hardensibility. With this modification the work material was similar to an oil hardening tool steel. Four pieces 6 inches long by 4½ inches wide and 1 inch thick were cut from a flat bar. All surface decarburization was removed and the flats sharpened and ground to ¾" thickness prior to heat treatment in a controlled atmosphere furnace. The test materials were quenched and tempered to 61½ to 62½ R<sub>c</sub>. All test surfaces were ground after heat treatment and a new surface was used for each fluid tested.

**Test specifications**

Machine: 6" x 18" Norton Surface Grinder, Hydraulic Table Feed.
Wheel speed: 5400 to 5800 s.f.p.m.
Cross feed: Approximately 0.50 in. per traverse.
Table speed: 26 feet/min. (Machine maximum)
Down feed: 0.001 and 0.002 in. per pass.
Fluid application: Approximately 1¼ gallons per minute, directed to grinding zone (maximum to avoid excessive splashing).

Grinding fluid: Tank (capacity 5 gallons) cleaned and flushed with clean tap water. Fluid mixed with tap water (moderate hardness) in concentration recommended by vendor for commercial preparations, and at a weight ratio of water to concentrate of 40:1 for the concentrate of Example I. 7½ gallons of mix prepared in plastic container.

With each change of fluid the first 2 quarts through the pump and line were discarded.

As can be readily determined from the results of Table HI, Composition B of this invention performed better than Composition X and Composition Y, and about equivalent to Composition Z in the tapping torque tests. Compositions A and B also passed the Herbert Rust Test and prevented the formation of rust on the grinder and work piece under the above test conditions. The examination of the grinder was conducted two days after completion of the actual grinding and revealed no new rust formation. The Herbert Rust Test is run by pouring the lubricant composition over cast iron chips and stirring every 5 minutes for 20 minutes. The test solution is then decanted and the chips allowed to stand in the inverted beaker for 48 hours after which the iron chips are examined for rust. Iron chips so treated with the cutting fluids of Example II exhibited no rust.
formation. When subjected to a foam test, which consists of diluting 1 part of the lubricant composition with 50 parts of water, shaking vigorously for one minute and then allowing to stand, Compositions A and B of Example II both showed good foam control with A showing the best performance. In about three weeks, B lost some foaming action while A remained almost unchanged. Composition X and Composition Y were found to have good foam control and Composition Z almost none. Also in the surface grind test Composition B settled 50-75% of the swarf, and in laboratory testing, Composition A settled finely more effectively than Composition B at 1:50 dilution. Composition X floated all swarf and Composition Y settled all of it. No tacky residue deposits were observed when Compositions A and B were allowed to evaporate on the grinders, while Composition Y and Composition X left a tacky residue. In a freeze and thaw test, solidification of Compositions A and B at 13.0°F over a 24-hour period did not occur, and restoration to original condition was complete in only 15 minutes at normal temperature. The freeze-thaw properties of Compositions A and B, therefore, are excellent.

Compositions A and B exhibited a very faint but pleasant odor, and rated fair for clarity. Composition Y also rated fair while Composition X and Composition Z rated excellent for clarity. Only a trace of white substance appeared to settle out when Compositions A and B were diluted at 1:50 in hard water (1000 p.p.b. Ca.) and stored for three weeks, thus hard water resistance was good. Finally, Compositions A and B caused no skin irritation when tested with animals at normal working concentrations of 1:20 to 1:100.

It is claimed:

1. A lubricating composition comprising an aqueous solution containing a lubricating amount of a water-soluble amine salt of a copolymer resin and a minor, effective amount of a water-soluble extreme pressure lubricating agent, said amine salts being those of amines having boiling points above about 200°C, and said copolymer resin being selected from the group consisting of styrene-maleic anhydride copolymers having a styrene to maleic anhydride ratio of about 1:1 to 5:1 and a molecular weight of about 700 to 8000, and the about 25 to 100 percent halfesters of said styrene-maleic anhydride copolymers, in which the styrene-maleic anhydride copolymers are esterified with a water-soluble member having the structure

\[ R(OR')_2\text{OH} \]

wherein R and R' are aliphatic hydrocarbon radicals of about 2 to 6 carbon atoms, the total number of carbon atoms in R and a single R' is less than about 7, and x = 0 to about 12.

2. The composition of claim 1 comprising said minor effective amount of a water-soluble extreme pressure lubricating agent and about 1 to 40 weight percent of said copolymer resin, about 30 to 70 weight percent of said water-soluble amine which forms the amine salt of the copolymer and about 10 to 85 weight percent water.

3. The composition of claim 2 comprising about 1 to 10 weight percent of said copolymer resin, about 30 to 55 weight percent of said amine and about 10 to 50 weight percent water.

4. The composition of claim 1 in which the amine is triethanolamine or diethanolamine.

5. The composition of claim 3 in which the amine is triethanolamine or diethanolamine.

6. The composition of claim 2 in which the amine is triethanolamine or diethanolamine and the half-ester is the half-ester of a styrene-maleic anhydride copolymer having a molecular weight of about 1800 and a molar ratio of styrene to maleic anhydride of about 3 to 1 and methoxy polyethylene glycol of molecular weight about 350.

7. The composition of claim 1 which contains about 2 to 10 weight percent of the extreme pressure lubricating agent.

8. The composition of claim 6 which contains about 2 to 10 weight percent of the extreme pressure lubricating agent.

9. The composition of claim 7 in which the extreme pressure agent is an amine salt of a fatty acid of from 12 to 20 carbon atoms.

10. The composition of claim 8 in which the extreme pressure agent is an amine salt of a fatty acid of from 12 to 20 carbon atoms.

11. The composition of claim 7 in which the extreme pressure agent is a phosphate ester acid.

12. The composition of claim 8 in which the extreme pressure agent is a phosphate ester acid.

13. The composition of claim 9 in which the amine salt is triethanolamine or diethanolamine olate.

14. The composition of claim 10 in which the amine salt is triethanolamine or diethanolamine olate and the water-soluble amine is triethanolamine or diethanolamine.

15. The composition of claim 1 in which the half-ester is the 50 percent ethylene glycol monobutyl ether half-ester of styrene maleic anhydride copolymer having a mol. wt. of about 1600 and a molar ratio of styrene to maleic anhydride of 1:1.

16. The composition of claim 15 in which the amine is triethanolamine or diethanolamine.

17. The composition of claim 7 in which the amine is triethanolamine or diethanolamine.

18. The composition of claim 1 which contains about 1 to 10 weight percent of an alcohol of about 6 to 20 carbon atoms as an antifoaming agent, about 2 to 10 weight percent boric acid or other boron compound which forms boric acid on hydration; and up to about 30 weight percent of a compound selected from the group consisting of diethylene glycol monoethyl ether and polyethylene glycol of molecular weight up to 5000.

19. The composition of claim 17 which contains about 1 to 10 weight percent of an alcohol of about 6 to 20 carbon atoms as an antifoaming agent, about 2 to 10 weight percent boric acid or other boron compound which forms boric acid on hydration; and up to about 30 weight percent of a compound selected from the group consisting of diethylene glycol monoethyl ether and polyethylene glycol of molecular weight up to 5000.

20. The composition of claim 5 which contains about 1 to 10 weight percent of an alcohol of about 6 to 20 carbon atoms as an antifoaming agent, about 2 to 10 weight percent boric acid or other boron compound which forms boric acid on hydration; and up to about 30 weight percent of a compound selected from the group consisting of diethylene glycol monoethyl ether and polyethylene glycol of molecular weight up to 5000.

21. The composition of claim 1 in which the styrene-maleic anhydride copolymer has a molecular weight of about 700 to 3000.

22. The composition of claim 17 in which the styrene-maleic anhydride copolymer has a molecular weight of about 700 to 3000.

23. The composition of claim 18 in which the styrene-maleic anhydride copolymer has a molecular weight of about 700 to 3000.

24. A composition comprising an aqueous solution containing a lubricating amount of a water-soluble amine salt of a copolymer resin, an alcohol of about 6 to 20 carbon atoms as an antifoaming agent, boric acid or other boron compound which forms boric acid on hydration and a compound selected from the group consisting of diethylene glycol monoethyl ether and polyethylene glycol of molecular weight up to about 5000, said amine salts being those of amines having boiling points above about 200°C, and said copolymer resins being selected from the group consisting of styrene-maleic anhydride copoly-
1:1 to 5:1 and a molecular weight of about 700 to 80,000 and the about 25 to about 100 percent half-esters of said styrene-maleic anhydride copolymers, in which the styrene-maleic anhydride copolymers are esterified with a water-soluble member having the structure

\[ R(OH) \_x \_OH \]

wherein \( R \) and \( R' \) are aliphatic hydrocarbon radicals of about 2 to 6 carbon atoms, the total number of carbon atoms in \( R \) and a single \( R' \) is less than about 7, and \( x = 0 \) to about 12.

25. The composition of claim 24 which contains about 1 to 10 weight percent of the alcohol, about 2 to 10 weight percent of the boric acid or other boron compound and up to about 30 weight percent of the compound selected from the group consisting of diethylene glycol monooethyl ether and polyethylene glycol.

26. The composition of claim 11 in which the styrene-maleic anhydride copolymer has a molecular weight of about 700 to 3000.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,645,897 Dated February 29, 1972

Inventor(s) Howard D. Gower, Bob G. Gower and David W. Young

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 27, after "now abandoned" add —and copending application
Ser. No. 778,804, filed November 25, 1968.—

Column 3, line 53, reads "formation" should read —formulation—

Column 5, line 60, reads "grinned" should read —grinded—

Signed and sealed this 27th day of June 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR. ROBERT GOTTSCHALK
Attesting Officer Commissioner of Patents