United States Patent [19]

Parkinson

[11] **3,873,458**

[45] **Mar. 25, 1975**

[54] **RESIN-CONTAINING LUBRICANT COATINGS**

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[22] Filed: **May 18, 1973**

[21] Appl. No.: **361,727**

[52] **U.S. Cl.**.................... **252/49.5,** 252/11, 252/18, 252/34, 252/49.5, 252/56 R, 117/132 C, 72/42

[51] **Int. Cl.**......................... **C10m 1/06,** C10m 1/28

[58] **Field of Search**.......... 252/11, 16, 18, 34, 49.3, 252/49.5, 56 R; 117/132 C; 72/42

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[57] **ABSTRACT**

Composition for forming lubricant coating, particularly useful in processes for working of sheet metals, comprising a resin capable of forming a layer adhering to the surface, and an oil for forming an upper layer to enhance the lubricating properties on top of and/or partially distributed within the resin layer; and a method of applying both layers of the coating to the metal surface simultaneously from a single aqueous dispersion or emulsion composition. The coating has been found to greatly increase the ability of the metal sheet to withstand severe fabrication processes, such as deep-drawing, without tearing or galling, compared with ordinary lubricating oils or greases.

20 Claims, No Drawings

RESIN-CONTAINING LUBRICANT COATINGS

BACKGROUND OF THE INVENTION

In deep-drawing, or other severe forming processes for sheet metals, such as carbon steel or stainless steel, there is a need for a lubricant which would make it possible to fabricate parts without tearing or galling that would not be possible with ordinary lubricating oils or greases. Such a lubricant should allow the metal to flow more uniformly during the draw, so that stresses are more uniformly distributed and a more severe draw can be made without metal tearing or fracture. The lubricant should stay in place in areas of severe pressure and thus prevent galling or welding from metal-to-metal contact with the dies, as in ironing methods of metal forming.

The use of a resinous coating on metal underneath a layer of oil, soap, wax or grease is known to industry as a lubricant system for deep-drawing (e.g., "Milbond," H. A. Montgomery Company). However, this lubricant system must be applied in two step: (1) a resinous coating is applied and dried; (2) the oil or grease is applied in a second operation. Some other lubricant systems use a phosphate or similar conversion coating as the base to hold the lubricant oil or grease. These also are two-step operations in which the metal must first be treated and then the oil applied separately.

A one-step method of applying both the resin layer and the oil layer simultaneously from a single aqueous dispersion or emulsion would be advantageous because it would simplify the application process, and may also enhance the lubrication because the more intimate and uniform distribution of the oil phase over and throughout the resin layer.

SUMMARY OF THE INVENTION

I have developed a composition for the purpose of applying a compositie resin/oil lubricant coating on a substrate such as metal sheets in a single coating operation. When this composition is applied as a thin coating and dried, it separates into two layers or phases: (a) a tough resin layer tightly adhering to the substrate, and (b) an oil layer or phase, separated from the resin by mutual insolubility, covering the resin layer or dispersed therein.

The tough, adherent resin layer provides a barrier against galling of the metal under high pressure forming processes and intimately holds the "oil phase" that provides a lower coefficient of friction. The ability of this composition to distribute the two components in layers in proper relationship to the substrate in a single operation greatly simplifies the application process.

This resin/oil composite lubricant coating has been found to be particularly useful when preapplied and dried on metal sheets as a once-through lubricant for severe metal-forming processes such as deep-drawing, draw-and-iron processes, and roll-forming. (It is not recommended where the lubricant must be continually replaced, as in machine bearings.) In addition to its lubricating properties, this coating provides protection for the metal surface against corrosion and abrasion.

My compositions for applying the lubricant coating are aqueous dispersions consisting essentially of a "resin phase" and an "oil phase" in a single composition. For proper performance. the resin must be a tough polymer, which is dispersable in an aqueous medium, which has ability to form a film during the drying that adheres strongly to a metal substrate, which is insoluble in the oil phase, and which may easily be dissolved or stripped from the metal surface after use by a process such as alkaline detergent cleaning.

The preferred resins for my lubricating composition include ethyleneacrylic acid copolymers, particularly those with high carboxyl content (e.g., 18 to 24 percent) such as Union Carbide Corporation's "EAA 9300 or EAA 9500." Although either EAA 9300 may be used, a more stable emulsion is achieved with the higher molecular weight EAA 9300 copolymer solution. These copolymer resins may be dissolved in hot aqueous alkali to give a soap-like colloidal solution of the salt formed by a reaction similar to saponification. They remain in colloidal dispersion on cooling to room temperature. When a volatile alkali or base, such as ammonium hydroxide or certain volatile amines, is used to disperse the copolymer, the colloidal solution may be applied as a coating that, when dried to drive off the alkali, reconstitutes the original acid copolymer resin on the surface of the substrate. Such coatings have excellent adhesion to metals and are tough, flexible, and water-resistant; and they may be easily removed by redissolving in hot alkaline solutions such as those used as commercial metal cleaners. One advantage to such dispersions of ethylene-acrylic acid copolymers when used in my lubricating composition is that they are themselves excellent emulsifying or dispersing agents for the oil phase and other additives to the composition.

The resin phase of my composition may also contain other resins in addition to or instead of the above-mentioned ethylene-acrylic acid dispersion. Aqueous dispersions of other copolymers, terpolymers, or ionomers of ethylene with other ethylenically unsaturated acids, such as methacrylic or crotonic acids, or with ethylenically unsaturated esters, such as vinyl acetate, may be substituted for all or part of the ethylene-acrylic acid copolymer dispersion. Preferred esters of the acrylic acid and other ethylenically unsaturated acids are the lower esters of 1 – 4 carbon atoms. Other water-soluble or dispersible resins, such as polyvinyl alcohol, may also be incorporated as a minor portion of the resin phase. Polyvinyl alcohol was found to improve wetting and give a drier (less greasy) coating by encapsulating most of the oil in the resin, which may be advantageous for certain usages. However, polyvinyl alcohol has its disadvantages, such as, separation in storage as a gelatinous third-phase in my emulsion, giving coatings with poorer adhesion to the metal substrate, or more difficulty in removal with alkaline cleaners.

The second essential component of my lubricating coating composition is the "oil phase" which is required to reduce the friction of the lubrication coating. This oil phase may consist of a lubricant oil, by which I mean mineral oil, animal or vegetable oils or fats, fatty-acid soaps, greases, waxes, and other natural or synthetic lubricating materials or combinations thereof. In selecting material for the oil phase of my composition, it is desirable that in addition to having a low coefficiency of friction, it be insoluble in the resin phase so that the resin coating layer is not softened, that the oil separates from the resin phase during the drying of the dispersion coating, and that is does not interfere with the adhesion of the resin layer to the metal substrate.

In addition to the major resin/oil components, my composition may contain minor amounts of surfactants, solvents, thickeners, alkalis, and other material to improve the stability, wetting, defoaming, dispersion, viscosity, and coating characteristics of the emulsions and the uniformity, smoothness, thickness, and removability of dried coatings. Thickness of the coating may also be controlled by varying the amount of water vs. the total nonvolatile concentration of the emulsion, or by the means of application. For severe high-pressure metal-forming, it may be desirable to add finely-divided solid lubricants such as graphite, poly carbon monofluoride or molybdenum sulfide powders. Certain fillers selected for low abrasiveness, such as clay, talc, or mica, or oxide pigments may also be dispersed in the emulsion and may be advantageous in certain cases to strengthen the resin barrier layer of the coating. It is also possible to disperse powdered or emulsified polymers with low coefficient of friction, such as nylon or teflon, in the composition. I have found that my compositions are particularly effective in maintaining stable dispersions of such powdered solids with little settling in storage.

The composition for the application of my coating is preferably prepared by predissolving or dispersing the resins in an aqueous medium and then emulsifying or dispersing the "oil phase" into this resin dispersion by highshear mixing. Minor additions may be blended as desired.

For maximum effectiveness of lubrication, the "oil phase" nonvolatiles are preferably 25 to 75 percent by weight of the total nonvolatiles remaining in the coating after drying, although any amount of oil up to as much as 3 times the amount of resin may be blended in my composition. As little as one percent oil, based on the resin, may be desirable where drier coatings are preferred or where additional oil is being applied over the coating before fabrication.

The dispersion of my composition is prepared as a low-viscosity fluid (preferably 50 to 1000 centipoises) that may be easily applied to metal as a thin coating by conventional methods such as roll-coating, brushing, dipping, spraying, etc. The viscosity and concentration of the dispersion may be controlled by the amount of water added or by the addition of fillers, thickeners, or gelling agents to adjust desired thickness of the resulting dried coating. Concentrations of about 19 to 45 percent total resin/oil nonvolatiles in the dispersion have been found to be satisfactory for roll-coating. I have found that thin coatings, with a dried coating weight in the range of approximately 50 to 350 milligrams per square foot (0.54 to 3.77 grams per square meter) or approximately 0.5 to 3.0 micron thickness, give satisfactory lubricating properties to sheet steel. Heavier coatings up to 25 microns may be desirable for some applications.

After application, the coating is dried to evaporate the volatiles, such as water and ammonia. Drying at room temperature (for several hours) may be used, but it is preferred to dry with heat from about 120° C to about 200° C (for less than a minute.) Such heat-drying improves the adhesion of the coating to the metal. Over-heating may make some coatings more difficult to remove in subsequent alkaline cleaning.

EXAMPLES

EXAMPLE 1

(See Table I)

An aqueous ammonium solution of an ethylene-acrylic acid copolymer resin (containing about 20 percent acid) was prepared by heating the resin to 90° to 130° C in a pressure vessel, in a slightly more than stoichemetric amounts to ammonium hydroxide with sufficient water to give about 22 percent resin solids. A mixture of surfactants was added to improve the wetting properties, the emulsion stability, and foam reduction of the coating composition but were not essential. (A combination of an alkyl-phenoxy-polyethoxy-ethanol, a ditertiary acetylenic glycol and a dispersant, such as Tamol 731 (Rohm and Haas) or a lignosulfonate, were found to be satisfactory, but many other surfactants may be used.) In the proportions indicated in Table I (Example 1) a mixture of parafinic mineral oil and lard oil were blended into the ethylene-copolymer resin solution with high-shear mixing. The emulsion formed was quite stable. Creaming occurred with low molecular weight copolymer (EAS 9500) on storage, but was easily redispersed. Without further dilution, the total nonvolatiles were about 41 percent of the solution. This composition, when dried on steel sheets, gave a smooth coating with a tough layer of resin adjacent and tightly adhering to the steel, with most of the oil in a separate layer over the resin. When applied and dried on stainless steel sheet in coating weights of about 100 mg/ft^2 (1.08 g/m^2) to 350 mg/ft^2 (3.77 g/m^2) the depth of draw was increased 20 to 32 percent (to 0.550 to 0.600 inch) in the Olsen cup test (ASTM A344) compared to an average of about 0.450 inch depth with the same steel with a standard mineral oil lubricant. This lubricant coating was also applied to thin carbon steel sheets (blackplate) and fabricated sucessfully into cans by a draw-and-iron process without galling or tearing. Tin plating or special phosphate treatments of the steel have generally been necessary to obtain satisfactory draw-and-iron processing with ordinary lubricants. The coefficient of friction between this coating and steel was 0.077.

EXAMPLE 2

Molybdenum sulfide of a very fine particle size (0.35 μ average) was added to the composition of Example 1. An excellent dispersion with practically no settling in storage was obtained. The purpose of the addition was to improve resistance to galling under severe high-pressure fabrication conditions. The Olsen cup depth of draw and draw-and-iron results in laboratory tests were essentially the same as Example 1. It is expected that the MoS_2 addition may give superior performance under more severe fabrication conditions.

EXAMPLE 3

This composition was prepared by dissolving polyvinyl alcohol in hot water and then adding the ethylene-acrylic acid copolymer ammonium solution and emulsifying mixed lard oil and oleic acid into it. This composition gave smooth, adherent, dry coatings in which the oil appeared to be dispered in a matrix of resin. Coating of 52 to 104 milligrams per square foot (0.56 to 1.12 g/m^2) increased the Olsen draw depth by about 13 to 25 percent on stainless steel sheet. Carbon steel "blackplate" sheets coated with this composition were successfully draw-and-ironed into cans without galling in laboratory tests. Initial adhesion of these coatings to the steel was good, but after storage for several months this composition gave coatings with poor adhesion. The coefficient of friction between these coatings and steel was the same as Example 1 (0.077), but there was evidence that resistance to galling was inferior under very severe conditions.

EXAMPLE 4

In this composition an inorganic filler was added to the composition of Example 3. Both talc and a very fine iron oxide pigment were tried. Dispersants such as lignosulfonates and phosphates were effective in maintaining good suspension of the solids. Concentrations used are given in Table 1. With talc additions, there was evidence of slight improvement in resistance to galling in coatings on blackplate in draw-and-iron can tests on production equipment. However, iron oxide gave satisfactory results on laboratory equipment but caused excessive breakage and galling in more severe processes.

EXAMPLE 5

This example illustrates the substitution of another resin dispersion for a portion of the ethylene-acrylic acid copolymer solution. The ethylene"ionomer" dispersion (Elvax D1249, E. I. du Pont de Nemours Co.) is an ethylene-methacrylic acid copolymer partly neutralized with sodium hydroxide and dispersed by an emulsion polymerization process with surfactants. The performance of this composition as a lubricant coating was similar to that of Example 3.

EXAMPLE 6

This composition contains a soap (ammonium oleate) as the oil phase instead of mineral oil or fats. The composition was a uniform, translucent, stable, colloidal solution with good wetting properties but with a tendency to foam. Even when diluted to about 14 percent nonvolatile so that an extremely thin coating was applied, it was found that this composition gave a 13 percent improvement in Olsen cup depth on stainless steel compared with the same steel with a standard lubricating mineral oil.

EXAMPLE 7

Into an ammonium solution of ethylene-acrylic acid copolymer light mineral oil was emulsified with high-shear stirring. Sufficient water was added to dilute the mixture to about 24 percent nonvolatiles (of which about 70 percent was oil). This emulsion separated into two layers on standing but was easily redispersed for application. Applied to the same stainless steel as in Example 1, this coating improved the depth of Olsen draw by about 14 percent.

Table I

Typical Formulae for Lubricant Coating Materials (parts by weight)

	Examples 1	2	3	4	5	6	7
Resin Phase:							
Ethylene-acrylic acid copolymer (22% solids ammonium solution)	100	100	100	100	100	100	100
Polyvinyl Alcohol	—	—	6.7	6.7	9	—	—
Ethylene-ionomer dispersion (Elvax D1249) (42% solids)	—	—	—	—	30	—	—
Oil Phase:							
Mineral Oil	15	15	—	—	—	—	50
Lard Oil	15	15	30	30	45	—	—
Oleic Acid	—	—	3	3	4.5	—	—
Soap - ammonium oleate	—	—	—	—	—	25	—
Surfactants:	0.75	0.75	0.3	3.3	0.2	0.13	0.13
Fillers or Solid Lubricant:							
Talc or iron oxide	—	—	—	15	—	—	—
Molybdenum Sulfide	—	2.5 to 10.0	—	—	—	—	—
Water (To dilute to 14 to 40 percent nonvolatiles according to thickness of coating desired).							

My invention is not restricted to the above specific examples and illustrations. It may be otherwise practiced within the scope of the following claims.

I claim:

1. Process for cold forming or shaping metal comprising subjecting to deformation pressure against a solid surface metal which has been coated with a resin-oil layer by applying to its surface a single aqueous dispersion composition and drying said composition to remove water and other volatiles, said composition prepared by blending (a) a lubricant oil selected from mineral oil, animal or vegetable oils, fats, soaps, fatty esters, or other natural or synthetic oil, grease, or wax lubricant materials or mixtures thereof, and (b) a dispersion or solution of a normally solid copolymer of ethylene and acrylic acid, containing 15 to 25% acrylic acid, in water containing alkali sufficient to form a water-soluble or dispersable salt or ionomer of the copolymer, said lubricant oil comprising from about 1 to about 75% of the total nonvolatiles of the coating composition and being substantially insoluble in the resin.

2. Process of claim 1 in which the alkali for dissolving or dispersing the ethylene-acrylic acid copolymer is ammonium hydroxide or a volatile amine.

3. Process for cold forming or shaping metal comprising subjecting to deformation pressure against a solid surface metal which has been coated with a resin-oil

layer by applying to its surface a single aqueous dispersion composition and drying said composition to remove water and other volatiles, said composition prepared by blending (a) from about 1% to about 75% lubricant oil selected from mineral oil, animal or vegetable oils, fats, soaps, fatty esters, and other natural or synthetic oil or grease lubricant materials or mixtures thereof and (b) the balance an aqueous dispersion or latex of a normally solid copolymer or terpolymer of ethylene and vinyl acetate or methacrylic acid containing 60 to 85% ethylene, 0 to 40% vinyl acetate, and 0 to 25% methacrylic acid.

4. Method of forming metal comprising:

a. emulsifying a lubricating oil in an aqueous suspension of a normally solid copolymer terpolymer or ionomer derived from ethylene and an ethylenically unsaturated monomer selected from vinyl acetate, acrylic acid, methacrylic acid, and crotonic acid, their salts and lower esters, the ethylene comprising from about 50% by weight to about 95% by weight of the copolymer or ionomer, the weight ratio of copolymer or ionomer to lubricant oil being from about 100:1 to about 1:3, the lubricant oil being substantially insoluble in the ethylene copolymer or ionomer;

b. placing on metal to be formed a coating of the emulsion thereby made,

c. drying said coating, and

d. subjecting said metal to deformation pressure against a solid surface.

5. A process for cold-forming or shaping metal of claim **4,** in which a solid powder or solution, from a group consisting of graphite, molybdenum sulfide, poly carbon monofluoride, tetrafluorethylene, nylon, talc, and kaolin clay is dispersed or suspended in the resin/oil coating composition so that upon application to the metal and drying, the solid powder is distributed in and bound by the coating.

6. Method of claim **4** wherein the dried coating has an average weight of at least about 50 milligrams per square foot.

7. Method of claim **4** followed by the step of removing the coating from the formed metal by cleaning it with an alkaline detergent.

8. Method of claim **4** wherein said drying is accomplished at a temperature above the softening point of the resin but below the temperature that will cause significant decomposition or evaporation of the resin or oil in the time exposed.

9. Composition useful for forming lubricant coatings comprising an emulsion of a lubricant oil in an aqueous dispersion of a normally solid adhesive resin copolymer, terpolymer or ionomer of ethylene and an ethylenically unsaturated monomer selected from the group consisting of vinyl acetate, acrylic acid, methacrylic acid, crotonic acid, their salts and lower esters, said resin containing about 50% to about 90% by weight ethylene, the weight ratio of resin to lubricant oil being from about 100;1 to about 1:3, the lubricant oil being substantially insoluble in the resin.

10. Composition of claim **9** in which the adhesive resin is a copolymer of ethylene and vinyl acetate.

11. Metal coated with at least about 0.54 grams per square meter of a dried composition of claim **10.**

12. Composition of claim **9** in which the lubricant oil is mineral oil.

13. Metal coated with at least about 0.54 grams per square meter of a dried composition of claim **12.**

14. Composition of claim **9** in which the resin is an ionomer.

15. Metal coated with at least about 0.54 grams per square meter of a dried composition of claim **14.**

16. Composition of claim **9** in which the resin is a copolymer of ethylene and acrylic acid.

17. Method of lubricating surfaces comprising applying to said surface a composition of claim **9** and drying it to form a coating having an average weight range of at least 50 milligrams per square foot.

18. Metal coated with at least about 0.54 grams per square meter of a dried composition of claim **9.**

19. Method of making a composition useful for forming lubricant coatings comprising dispersing a copolymer of about 75 to about 85% by weight ethylene and about 15 to about 25% acrylic acid in water containing a volatile alkali, and emulsifying a lubricant oil in the resulting dispersion, the ratio of copolymer to lubricant oil being about 100:1 to about 1:3.

20. Method of claim **19** in which the volatile alkali is ammonium hydroxide.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,873,458 Dated March 25, 1975

Inventor(s) Robert E. Parkinson

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

Column 2, line 9, after "EAA 9300", second occurrence, insert -- or EAA 9500 --.

Signed and Sealed this

twenty-second Day of *July 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks