(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 073 306**
B1

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **09.04.86**

(51) Int. Cl.⁴: **C 10 M 111/06** // C10N40/20

(21) Application number: **82105093.7**

(22) Date of filing: **11.06.82**

(54) **Cold forming lubricants and process.**

(30) Priority: **19.08.81 US 294259**
06.01.82 US 337219

(43) Date of publication of application:
09.03.83 Bulletin 83/10

(45) Publication of the grant of the patent:
09.04.86 Bulletin 86/15

(84) Designated Contracting States:
BE DE FR GB NL SE

(56) References cited:
FR-A-1 498 978
GB-A-1 349 475
US-A-3 375 193
US-A-3 983 044

The file contains technical information submitted after the application was filed and not included in this specification

(73) Proprietor: **PENNWALT CORPORATION**
Pennwalt Building Three Parkway
Philadelphia Pennsylvania 19102 (US)

(72) Inventor: **Atkiss, Thomas C.**
1017 School House Road
Pottstown, PA 19041 (US)
Inventor: **Corcoran, Leo F.**
1017 Sanderling Circle
Audubon, PA 19464 (US)

(74) Representative: **Kraus, Walter, Dr. et al**
Patentanwälte Kraus, Weisert & Partner
Thomas-Wimmer-Ring 15
D-8000 München 22 (DE)

EP 0 073 306 B1

Courier Press, Leamington Spa, England.

Description

This invention relates to a dry film lubricant system comprising a zinc phosphate coating on steel or aluminum. Moreover, the present invention relates to a process for cold forming ferrous and non-ferrous metals such as steel, stainless steel, copper and aluminum.

In the cold extrusion, drawing or forming of metal parts, a current practice is to prepare the parts by applying a zinc phosphate coating to the parts and then applying a dry film lubricant or a reactive lubricant to the zinc phosphate coating. Dry film lubricants are products containing soap and borax as their major constituents. Such lubricants are applied from an aqueous solution at high temperatures (greater than 60°C to boiling) and then dried on the metal surface. Dry film lubricants generally are used for mild forming operations.

Reactive stearate lubricants are also applied from aqueous solution. They consist of solutions of sodium stearate which are controlled in such a way that they react with the zinc phosphate coating to form zinc stearate within the crystal lattice of the coating. This provides a tightly bonded lubricant system which performs well in many severe cold extrusion applications.

Both lubricant systems offer the advantage of a dry, hard film which is not easily physically removed from the metal surface. This leads to a cleaner and safer work environment because oils tend to run off treated parts and coat the work area. However, there are some severe cold forming applications where neither system will perform adequately. At such times the use of an additional lubricant (such as molybdenum disulfide) or additional processing steps are required, both of which lead to additional expense.

We have attempted to employ additives to a reactive stearate lubricant which additives included a mica pigment, a dispersant for the mica, sulfurized oleic acid and a phosphate ester to provide a severe cold forming lubricant system. The mica pigment was added to improve the ability of the lubricant to function adequately in a severe cold forming process. However, it was found that in a manufacturing environment, such a lubricant system failed to work satisfactorily due to the settling of the mica from the coating bath and the use of such a system was abandoned.

We have now found that certain severe cold forming applications can be accomplished without need of a pigment and in some applications the need for a phosphate precoat has been eliminated.

GB—A—1 349 475 and FR—A—1 498 978 describe lubricating compositions comprising an aqueous pigment-free bath containing an alkali metal fatty acid with 8 to 22 carbon atoms and phosphate esters of polyethoxy ethers. From US—A—3 983 044 it is known to use chlorinated or sulfurized fatty acids as extreme pressure additives in water based lubricants for the cold forming of metals.

In accordance with this invention, there is provided a dry film lubricant system comprising a zinc phosphate coating on steel or aluminum which is characterized by the fact that the coating has been reacted with an alkali metal stearate and a compound selected from the group consisting of sulfurized fatty acids and chlorinated fatty acids, and mixtures thereof to provide a dry, pigment-free lubricant film.

Moreover, in accordance with this invention a process for cold forming steel or aluminum is provided which is characterized by applying to a steel or aluminum billet a coating of zinc phosphate, applying to the zinc phosphate a second pigment-free coating which includes an alkali metal stearate and an additive selected from the group consisting of sulfurized fatty acids and chlorinated fatty acids, and mixtures thereof from an aqueous bath so as to form a dry pigment-free lubricant film including a zinc soap and then forming the billet using a die.

Further, in accordance with this invention, there is provided a process for cold forming metals which is characterized by applying to the metal billet a pigment-free coating which includes an alkali metal fatty acid soap and an additive selected from the group consisting of sulfurized fatty acids, chlorinated fatty acids, and mixtures thereof from an aqueous bath so as to form a dry, pigment-free lubricant film and then forming the billet using a die.

The lubricant system and process of the invention are suitable for extreme cold forming operations where reductions of 35% or more are necessary in forming metal parts. The metal parts are dipped in a heated aqueous lubricant bath for several minutes, removed and dried to provide a hard dry lubricant film. Optionally, ferrous or aluminum parts are first provided with a zinc phosphate coating having a coating weight of approximately 1.6 to 3.2 mg/cm^2 as is conventional. The parts are next dipped in a reactive lubricant bath of the invention which contains an alkali metal stearate, for several minutes. The zinc coating reacts with the bath and, upon drying, a hard, dry lubricant film is formed on the part.

The lubricant system of the present invention includes an alkali metal stearate and an additive compound selected from the group consisting of sulfurized fatty acids, chlorinated fatty acids, and mixtures thereof. The sulfurized and chlorinated fatty acids are derived from unsaturated fatty acids and esters having 12 to 22 carbon atoms in the acid carbon chain, such as oleic, linderic, erucic, linoleic, linolenic, etc. acids by reacting the unsaturated bonds with sulfur or chlorine. As used herein, the terms chlorinated and sulfurized fatty acids include esters thereof. Such materials are available from Keil Chemical Division, Ferro Corp. as "sulfur bases" and "chlorinated fatty compounds" and have been traditionally used as additives to fluids for their extreme pressure lubricating properties in metal working applica-

tions such as cutting oils, water soluble soaps and drawing compounds but not as lubricant additives for forming dry hard films as in our invention. Additionally, the lubricant system may contain an phosphate ester of polyoxyethylene based non-ionic surfactants. The phosphate esters are sold as extreme pressure lubricants and are available under the trademark Antara® from GAF Corporation. They comprise a phosphate radical on a polyethyleneoxy non-ionic surfactant base. The non-ionic surfactant base consists of a hydrophobe and polyoxyethylene.

In one aspect of the invention, it is believed that an important attribute of the additive material is that it has an acid group which can react with the zinc phosphate to form a water insoluble zinc soap which is chemically bonded to the surface of the metal. The combination of these additives and the stearate provide a dry film with unique lubricating properties which permits the cold extrusion of certain metal parts. The forming temperatures are reduced so that the parts are not heat damaged and the lubricating system avoids various other operating problems such as sticking in the die.

Because of the added acidity due to the lubricant additives, the free acidity of the bath must be adjusted to assure reaction of the ingredients of the bath with the zinc phosphate coating when a phosphate precoat is used. The adjustment also is used to control the viscosity of the bath. The "free fatty acid" is adjusted by adding a base such as NaOH so as to be within the range of ±1.0 with ±0.5 preferred. Free fatty acid is determined by placing 100 ml of 190 proof ethyl alcohol in a 250 ml. Erlenmeyer flask and adding five drops of phenolphthalein indicator. Sodium hydroxide (0.1 N) is added dropwise until a faint pink color develops. A 10 ml. portion of the lubricant bath is pipetted into the alcohol and the alcohol is heated to boiling. While hot, the alcohol solution is titrated to a pink endpoint with the 0.1 N NaOH and the amount of NaOH used is recorded as the "free fatty acid points" where 1 ml.=1.0 point. If the solution is pink after boiling then it is titrated with 0.1 N sulfuric acid until the pink color is discharged. The amount of H_2SO_4 used is the "free alkali points" where 1 ml.=1.0 alkali point or −1.0 acid point.

The amount of lubricant additive employed will depend upon the application and generally can range from about 1—30 parts by weight per 100 parts of the total combined weight of fatty acid soap and additive combined. A sufficient amount is used to provide the required lubrication for a given application. Amounts of additive above about 30 parts by weight make the lubricant coating film soft.

The solution concentration can range from about 2 to 10% by weight and preferably 4 to 8% by weight "total fatty solids". Total fatty solids are determined by pipetting a 20 ml sample of the bath into an 18 gram Babcock type test bottle. A 25 ml portion of concentrated sulfuric acid is then added and the bottle is shaken until the fatty matter separates. The liquid sample is diluted with 50% aqueous H_2SO_4 until the volume of separated fatty matter can be read on the graduated neck of the bottle directly as percent fatty solids.

The bath of the invention is formed and maintained by adding the ingredients with mixing to hot water (71°C or above), otherwise the fatty acid portion will separate.

The compositions and process of the invention are further illustrated by, but are not intended to be limited to, the following examples wherein parts are parts by weight unless otherwise indicated.

Examples 1—4

Four different lubricating baths were used to form a hard, dry film lubricant coating on the surface of steel billets to be formed into hose couplings by cold forward extrusion. The billets were cylindrical tubes with a length of about 6.35 cm and a diameter of about 1.27 cm. The billets were formed into hose couplings by cold forward extrusion where one end of the billet was reduced to provide a 17.8 cm long section of 2.54 cm in diameter with a wall thickness of about 0.32 cm extending from about a 2.54 cm long section of billet of the original dimensions. A zinc phosphate coating was first formed on the billet and then the billets were dipped for 5 minutes in the reactive lubricant bath, which was at a temperature of about 71—77°C, removed and allowed to dry. The bath compositions are given in Table I below:

TABLE I

Ingredient	Composition in parts by weight			
	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Sodium Stearate	220	220	160	160
Sulfurized Oleic Acid*	44	66	16	16
Water	4000	4000	4000	4000
NaOH (50% wt.%)	10	14	5	6
Phosphate Ester of polyoxyethylene**	0	0	45	0

* Base 44, (Keil Chemical Division Ferro Corp.); Sulfur, 14%; Active Sulfur, 5%; Viscosity @ 37.8°C SUS 2400, @ 99°C SUS 200; wt g/l @ 15.6°C 1008 No. 175.

** Antara LP-700 (GAF Corp.); phosphate radical on a polyethyleneoxy non-ionic surfactant base; Water Soluble liquid; s.g. 25°C 1.20; moisture 0.5% max; pH (10% in H_2O) 1.5—2.5; Acid No. 140—160; phosphorous 5.8% max.

The cold forming operation to produce the couplings involved a severe (about a 50%) reduction. Previous attempts to form the part using a standard zinc phosphate coating which had been reacted with sodium stearate were unsuccessful in forming the part. A modified dry film of soap and borax was successful in forming the part without use of phosphate coating but resulted in excessive heat generation and, due to its hygroscopic nature, many operating problems. Each of the compositions shown in Table I allowed the parts to be successfully extruded at lower temperatures (at least −12°C) with the compositions of Example 3 and 4 appearing to give the best results.

Example 5

The composition of Example 4 was used to coat 400 steel billets for deep drawing steel grenades. The billets were cleaned in a caustic solution, rinsed with water, dried, immersed in the lubricant bath at a temperature of 79.4—82.2°C for about 5 minutes and then removed from the bath and dried. The bath had a total fatty solids content of 7 to 9% and a free fatty acid content of about 0.5 point. The billets were subjected to four cold forming operations, with cleaning, annealing and lubricant application between each forming operation, to successfully form the grenades. The acceptance rate was 96.5% which is slightly above the normal rate. The process previously used a phosphoric acid reactive oil which was messy to use and corrosive to the skin.

Example 6

The composition of Example 4 was used to coat aluminum billets for forming fire extinguisher bottles by impact extrusion. The aluminum billets were first cleaned in an alkaline solution, rinsed with water, alkaline etched, and rinsed with water. A number of the billets were coated with zinc phosphate, rinsed with water and an alkaline solution, coated with the lubricant composition of Example 4 at a bath concentration of about 8 percent by weight total fatty solids at temperatures of about 75.6—82.2°C and dried. The remaining billets were coated with lubricant without applying the zinc phosphate coating. It was noted that a reaction of the lubricant with the aluminum surface occurred even in the absence of the zinc phosphate undercoat. Both groups of billets were successfully impact extruded. Some die pick up resulted from the phosphate coated parts which could be remedied by lowering the coating thicknesses by adjusting the bath concentrations. The process previously used to form the bottles included a zinc phosphate undercoat and a soap type lubricant.

The process and compositions of the invention thus provide a non-oily, non-hygroscopic, dry, hard lubricant system which permits the severe cold forming of parts without die sticking and without damage or discoloration of the parts due to excessive temperature generation. The lubricant system is so effective that, as illustrated above, the use of a phosphate precoating can be eliminated in certain severe applications which reduces process stops and the possibility of die pick up of the lubricant.

Claims

1. A dry film lubricant system comprising a zinc phosphate coating on steel or aluminum, characterized by the fact that the coating has been reacted with an alkali metal stearate and a compound selected from the group consisting of sulfurized fatty acids and chlorinated fatty acids, and mixtures thereof to provide a dry, pigment-free lubricant film.

2. The dry film lubricant system of claim 1, characterized by the fact that the coating has been reacted additionally with a phosphate ester of a polyoxyethylene based non-ionic surfactant.

3. A process for cold forming steel or aluminum, characterized by applying to a steel or aluminum billet a coating of zinc phosphate, applying to the zinc phosphate a second pig-

ment-free coating which includes an alkali metal stearate and an additive selected from the group consisting of sulfurized fatty acids and chlorinated fatty acids, and mixtures thereof from an aqueous bath so as to form a dry pigment-free lubricant film including a zinc soap and then forming the billet using a die.

4. The process of claim 3, characterized by the fact that the second pigment-free coating additionally contains a phosphate ester of a polyoxyethylene based non-ionic surfactant.

5. A process for cold forming metals, characterized by applying to the metal billet a pigment-free coating which includes an alkali metal fatty acid soap and an additive selected from the group consisting of sulfurized fatty acids, chlorinated fatty acids, and mixtures thereof from an aqueous bath so as to form a dry, pigment-free lubricant film and then forming the billet using a die.

6. The process of claim 5, characterized by the fact that the pigment-free coating additionally contains a phosphate ester of a polyoxyethylene based non-ionic surfactant.

Patentansprüche

1. Trockenfilm-Schmiermittelsystem, umfassend einen Zinkphosphatüberzug auf Stahl oder Aluminium, dadurch gekennzeichnet, daß der Überzug mit einem Alkalimetallstearat und einer Verbindung, ausgewählt aus der Gruppe, bestehend aus sulfurisierten Fettsäuren und chlorierten Fettsäuren und Gemischen davon, umgesetzt worden ist, um einen trockenen, pigmentfreien Schmiermittelfilm herzustellen.

2. Trockenfilm-Schmiermittelsystem nach Anspruch 1, dadurch gekennzeichnet, daß der Überzug zusätzlich mit einem Phosphatester eines nichtionogenen oberflächenaktiven Mittels auf Polyoxyethylenbasis umgesetzt worden ist.

3. Verfahren zur Kaltverformung von Stahl oder Aluminium, dadurch gekennzeichnet, daß man auf einen Stahl- oder Aluminiumbarren einen Überzug aus Zinkphosphat aufbringt, auf das Zinkphosphat aus einem wäßrigen Bad einen zweiten pigmentfreien Überzug aufbringt, der ein Alkalimetallstearat und ein Additiv, ausgewählt aus der Gruppe, bestehend aus sulfurisierten Fettsäuren und chlorierten Fettsäuren und Gemischen davon, einschließt, um einen trockenen pigmentfreien Schmiermittelfilm zu bilden, der eine Zinkseife einschließt, und daß man sodann den Barren unter Verwendung eines Preßgesenks verformt.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß der zweite pigmentfreie Überzug zusätzlich einen Phosphatester eines nichtionogenen oberflächenaktiven Mittels auf Polyoxyethylenbasis enthält.

5. Verfahren zur Kaltverformung von Metallen, dadurch gekennzeichnet, daß man auf den Metallbarren aus einem wäßrigen Bad einen pigmentfreien Überzug aufbringt, der eine Alkalimetallfettsäureseife und ein Additiv, ausgewählt aus der Gruppe, bestehend aus sulfurisierten Fettsäuren, chlorierten Fettsäuren und Gemischen davon, einschließt, um einen trockenen pigmentfreien Schmiermittelfilm zu bilden, und daß man sodann den Barren unter Verwendung eines Preßgesenks verformt.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß der pigmentfreie Überzug zusätzlich einen Phosphatester eines nichtionogenen oberflächenaktiven Mittels auf Polyoxyethylenbasis enthält.

Revendications

1. Composition de lubrifiant en film sec comprenant un revêtement de phosphate de zinc sur de l'acier ou de l'aluminium, caractérisée par le fait que le revêtement a été amené à réagir avec un stéarate de métal alcalin et un composé choisi dans le groupe consistant en acides gras sulfurés et en acides gras chlorés et leurs mélanges, de manière à former un film sec de lubrifiant dépourvu de pigment.

2. Composition de lubrifiant en film sec suivant la revendication 1, caractérisée par le fait que le revêtement a été amené à réagir en outre avec un ester d'acide phosphorique d'un surfactant non ionique à base polyoxyéthylénique.

3. Procédé d'usinage à froid d'acier ou d'aluminium, caractérisé par l'application à une billette d'acier ou d'aluminium d'un revêtement de phosphate de zinc, l'application au phosphate de zinc d'un second revêtement dépourvu de pigment qui comprend un stéarate de métal alcalin et un additif choisi dans le groupe formé d'acides gras sulfurés et d'acides gras chlorés et de leurs mélanges, en bain aqueux de manière à former un film sec de lubrifiant dépourvu de pigment comprenant un savon de zinc, puis à usiner la billette en utilisant une matrice.

4. Procédé suivant la revendication 3, caractérisé par le fait que le second revêtement dépourvu de pigment contient en outre un ester d'acide phosphorique d'un surfactant non ionique à base polyoxyéthylénique.

5. Procédé d'usinage à froid de métaux, caractérisé par l'application à la billette métallique d'un revêtement dépourvu de pigment qui comprend un savon d'acide gras de métal alcalin et un additif choisi dans le groupe formé d'acides gras sulfurés, d'acides gras chlorés et de leurs mélanges, dans un bain aqueux de manière à former un film sec de lubrifiant dépourvu de pigment, puis à usiner la billette en utilisant une matrice.

6. Procédé suivant la revendication 5, caractérisé par le fait que le revêtement dépourvu de pigment contient en outre un ester d'acide phosphorique d'un surfactant non ionique à base polyoxyéthylénique.