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METHOD AND COMPOSITION FOR PREPARING FERROUS METAL FOR FORMING

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This invention relates to a method and composition for preparing ferrous metal for forming operations such as die forming and stamping of sheet stock, cold heading, and drawing of wire, rod and tubular stock, and the like.

As fully set forth in United States Letters Patent Reissue No. 23,184, reissued on December 20, 1949, to R. A. Whitbeck, it has been found desirable in the forming of metal stock to dispense with the usual wet lubricants and instead to coat the stock with a dry, homogeneous, self-adherent, lubricating and protective film which is readily removable, then to form the coated stock, in the absence of any additional lubricant, and to remove the film from the formed stock after which the formed stock is ready for painting, plating and the like. The film thus formed of alkaline material adheres to the stock due to a mechanical bond.

On very smooth surfaces, such as bright cold rolled steel, bright finish stainless steel, and steel stock which has been polished and buffed, difficulty occasionally is encountered with draws of very sharp radii due to a tendency, in such instances, for the lubricating film to shear off of the stock along the areas of sharp radius and build up on the dies. In due course, the lubricating material so built up on the dies sometimes causes a slight pattern on the steel and must be removed.

In such extreme cases the difficulty can be overcome by slightly etching the metal before coating with the lubricating film, or by coating the metal stock with a very thin porous coat which can be chemically removed, so as to provide better mechanical adhesion with the lubricating and protective film.

The advantages of this type of lubricating film and the procedures made possible thereby are fully set forth in the above reissue patent.

The present invention relates primarily to a method and composition for providing on the stock a chemically bonded microporous film by which better adhesion of the lubricating and protective film is obtained.

The invention also relates to a method and composition by which there is provided on the stock a microporous chemically bonded film which in itself is lubricating and which can be removed readily from the stock, the stock being lightly etched and coated in a single bath with a chemically bonded film containing sufficient lubricant so that the stock can be formed in the absence of any additional lubricant, thus dispensing with the need for the subsequent application of a lubricating and protective film such as described in the above reissue patent.

Referring first to the provision of the chemically bonded microporous film, which in itself is non-lubricating, the metal to be treated is first cleaned in any suitable manner, such as by an alkaline bath or by solvents, so that it is free from oleaginous material and other organic soils. The cleaned stock is then subjected to an aqueous bath of oxalic acid, phosphoric acid of 85% concentration, and hypophosphorous acid of 50% concentration. An example of a very satisfactory bath which is useful

throughout a wide range of operating conditions and for a wide range of ferrous metals is as follows:

Example I

	Preferred	Range
Oxalic Acid	about 25 parts	about 10 to 30 parts.
Phosphoric Acid (85% concentration).	about 10 parts	about 5 to 15 parts.
Hypophosphorous Acid (50% concentration).	about 1 part	about 1 part.
Water	about 1,000 parts	about 250 to 5,000 parts.

Additional specific examples are as follows:

Example II

For thin films:
Oxalic acid—about 10 parts
Phosphoric acid—about 10 parts
Hypophosphorous acid—about 1 part
Water—same as in Example I.

Example III

For thick films:
Oxalic acid—about 25 parts
Phosphoric acid—about 5 parts
Hypophosphorous acid—about 1 part
Water—same as in Example I

The ferrous stock is subjected to the aqueous solution by dipping or the like for approximately three minutes with the solution at a temperature from 200 to 205 degrees Fahrenheit. The reaction of the bath on the metal is very rapid for about one to one and one-half minutes and thereafter gradually decreases, becoming negligible at the end of three minutes. As a result of this treatment there is formed on the stock a microporous film which is chemically bonded to the metal.

The above example is one particularly suitable for bright cold rolled steel and high finish stainless steel but the example is not in limitation of the composition, proportions, or method, as wide variations may be made in each depending upon the type of ferrous metal, the alloying ingredients, the amount of impurities in the metal, the type of surface desired in the finished article, and the time factor which may be dictated by other procedures in the particular plant.

In order to inform others how to vary the composition and the method of application for the particular results desired and for better coordination with their existing practices, the function of the ingredients and the changes resulting from variations in the proportions, concentrations and the like are now pointed out.

The oxalic acid appears to react with the iron to form an iron oxalate film which is bonded chemically to the stock. The phosphoric acid etches the steel, thus assisting in the formation of the oxalate film and assuring an effective bond. The hypophosphorous acid is used as an accelerator, accelerating both the etching action and the film forming action.

Further, from the examination of the resultant film, it appears that the phosphoric acid probably cooperates with the oxalic acid to produce an iron phospho-oxalate film. In any event the film is microporous and chemically bonded to the surface of the stock.

After the treatment in the manner described, the stock is ready for the application of coatings, such as lubricating coatings, and for drawing in lubricated condition. As a lubricant, it is preferred to use the lubricating and protective coating described in the above reissue patent but other lubricants may be used as the microporous structure of the film retains the lubricant in place.

As the proportion of oxalic acid is decreased the rate of formation of film is decreased. As the oxalic acid is increased the rate of film formation is increased and this increase can proceed to such an extent that the rate of film formation is so disproportionate to the rate of etching that the film tends to become powdery and insufficiently adherent.

As the phosphoric acid is decreased the rate of etching of the metal is decreased and this likewise can result in an improper balance between etching and film formation. As the phosphoric acid is increased the rate of etching is increased and, unless there is a sufficiently high concentration of oxalic acid, the metal surface becomes etched disproportionately and to too great a degree before a sufficient film is formed.

An increase in the concentration of the soluble ingredients in the bath results in faster reactions whereas a decrease in the concentration slows down the reactions.

As the proportion of hypophosphorous acid is decreased, all reactions are slowed down and the time factor becomes controlling. In fact, without an accelerator an impractically long time is required. An increase in the accelerator results in a waste of the accelerating material.

In general, for a given type and thickness of film for a given ferrous metal, if the amount of oxalic acid is increased, the phosphoric acid likewise should be increased proportionately so as to maintain a balance between the rate of etching and the rate of film formation for the particular stock.

The concentration of these ingredients and their proportions depends largely on the type of steel or steel alloy, the kind of etch and the type of film desired. For example, in some metals a light etch with a relatively heavy film might be desirable whereas in others a heavier etch with a lighter film may be desirable and all degrees of relations between the type of etch and type of film may be obtained.

If a much more concentrated aqueous bath is employed, for example, about 250 parts of water instead of 1,000 parts with the amount of soluble ingredients remaining the same as described heretofore, the bath works effectively but since the bath becomes contaminated with iron due to the flocking of the iron, an unduly concentrated bath results in a waste of chemicals with no appreciable offsetting benefits. In fact, the more dilute the bath can be while still providing the desired film and etch, the better.

If the amounts of soluble ingredients remain the same and the water is increased to about 5,000 parts, there is a very rapid drop in the rates of reactions and too much time is required for obtaining the results. Preferably, therefore, with the other ingredients remaining in about the amounts recited in the example, water in an amount from about 800 to 1200 parts is preferred.

In general the phosphoric acid should be used in a proportion of not less than about 1 part of phosphoric acid to 5 parts of oxalic acid and not more than about 1 part of phosphoric acid to 1 part of oxalic acid. The hypophosphorous acid is preferably kept in about the ratio of 1 part to 10 parts of phosphoric acid.

Instead of oxalic acid, zinc phosphate or zinc oxalate or combinations thereof may be used for all or part of the oxalic acid. When either is so used, it should be substituted for the oxalic acid in the ranges recited in the ratio of about 3 parts of zinc phosphate or oxalate for 5 parts of oxalic acid.

Thus, films satisfactory for many purposes can be formed by subjecting the ferrous metal to an aqueous acid bath of material which, in the aqueous acid bath, reacts with the iron to produce complex iron compounds which are insoluble in the bath.

If it is desired to provide not only a microporous chemically bonded film but a film which in itself is lubricating, the same procedure as used above may be followed except that there is added to the bath a lubricant which is non-reactive with respect to the bath. The lubricant preferably is one, or a combination of two or more of the acid soluble esters of complex alcohols such, for example, as polyethylene glycol phosphate, glycerol borate, glycerol phosphate, and glycol borate.

More specifically, the esters may be acid-soluble aliphatic polyhydric alcohol esters having less than four hydroxy groups of inorganic acids.

The polyethylene glycol phosphate is preferred. If one or more of these lubricating ingredients is used with polyethylene glycol phosphate, the latter should be at least about one-half of the total of the esters.

Thus the lubricant may be polyethylene glycol phosphate and one or more of the group consisting of glycerol phosphate, glycerol borate, and glycol borate.

If the polyethylene glycol phosphate is not employed, there is a tendency toward tackiness of the resultant film and a moist film results. However, metallic salts of iron, manganese, zinc, lead and the like may be added so that the film can be dried. The salts are added in an amount equal to about one-fourth of the amount of phosphoric acid employed in the bath.

The procedure with the bath for lubricating films is the same as that used for non-lubricating films. The coated stock may be drawn while the film is only partially dry or fully dry. When full drying is required after subjection of the metal to the bath, the drying time is varied, depending upon the particular lubricating effect desired. If the lubricant to be added is polyethylene glycol phosphate, it is readily obtained as follows: A polyethylene glycol, ($OHCH_2(CH_2OCH_2)_xCHOH$), such as is readily available on the market under the name Carbowax 4000 or Carbowax 6000, which is solid at room temperature is melted. To this melted polyethylene glycol there is added phosphoric acid at 85% concentration, these two ingredients being in the ratio of about 100 parts of polyethylene glycol to about 5 parts of the phosphoric acid. This mixture is then heated to about 350 degrees Fahrenheit for about 30 minutes, after which is allowed to cool. As a result a solid hard waxy material is obtained and appears to be a polyethylene glycol phosphate. To the bath heretofore described, from about 5 to 15 parts, preferably about 10 parts, of this material is added. Thus a satisfactory bath would comprise:

	Preferred	Range
Oxalic acid	about 25 parts	about 10 to 30 parts.
Phosphoric acid (85% concentration).	about 10 parts	about 5 to 15 parts.
Hypophosphorous acid (50% concentration).	about 1 part	about 1 part.
Polyethylene glycol phosphate.	about 10 parts	about 5 to 15 parts.
Water	about 1,000 parts	about 250 to 5,000 parts.

As the amount of the lubricant is decreased, the lubricity decreases. As the amount of the lubricant is increased, the lubricity increases and the film gradually tends to, and finally becomes, tacky. The stock may be exposed in the bath for about 3 minutes at a temperature of about 200 to 205 degrees Fahrenheit after which it is removed. It may be drawn while the film is moist and partially dry or fully dry. In faces where drying is desired, for very thin films, drying at about 200 to 205 degrees Fahrenheit is satisfactory and for thicker films, of the same type, the coated stock should be dried at the same temperature but for a longer time. The resultant film is slippery, highly tenacious. It has no tendency to build up on the dies at sharp radii under the heat of forming.

By drying at a temperature of 400 to 450 degrees Fahrenheit, however, a different type of dry film is obtained. Such temperatures do more than merely dry the coating. During such drying the coating changes from its original deep green to light green indicating a

chemical change in the metallic film itself. Possibly this is due to change of the compound from a ferrous to a ferric state, that is, the changing of the film from a ferrous phospho-oxalate to a ferric phospho-oxalate, which latter is much more stable. At least it is known that if like pieces of stock are coated in the same manner and one is dried at 200 to 205 degrees Fahrenheit and the other at 400 to 450 degrees Fahrenheit, the resultant film on the latter is harder to break down and remove both mechanically and chemically than the former.

In any of the above examples, some additional substitutions can be made. For example, hydrogen fluoride may be substituted in whole or part for oxalic acid but in the examples given the hydrogen fluoride would be substituted in an amount of about one part of hydrogen fluoride for five parts of oxalic acid. If hydrogen fluoride is used to the exclusion of oxalic acid, etching only is obtained. Since this substitute formula provides a deeper etch the rough surface of the metal is depended upon for holding a subsequently applied lubricating film. It does not provide a chemically bonded film. Such is desirable for etching high silicon steels.

Where combined etching and microporous film is desired some oxalic acid, zinc phosphate or zinc oxalate, or combinations of two or more thereof must be added. In those instances wherein both the etch and microporous film are to be obtained, the metal may be exposed in the solution until the reaction runs to completion without deleterious effects.

In connection with all of the above compositions and procedures, after forming or drawing the stock, the film is removed by dipping the stock in a strong aqueous acid solution employing inorganic acids after which the formed stock is rinsed and dried.

Where the word "parts" has been employed hereinbefore and in the appended claims to denote the amount of ingredients to be used in formulating the compositions, it is to be understood that the parts are by weight.

Having thus described our invention, we claim:

1. A composition to be dissolved in water to provide an aqueous bath for applying to ferrous metal stock to form thereon a microporous lubricating film which is chemically bonded to the stock and consisting essentially of the following:

A material selected from the group consisting of oxalic acid, zinc oxalate, and zinc phosphate, and mixtures of the foregoing	About 10 to 30 parts.
Acid-soluble, aliphatic polyhydric alcohol ester having less than four hydroxy groups of an inorganic acid	About 5 to 15 parts.
Phosphoric acid (about 85% concentration)	About 5 to 15 parts.
and	
Hypophosphorous acid (about 50% concentration)	About 1 part.

2. A composition according to claim 1 characterized in that said ester is polyethylene glycol phosphate.

3. A composition according to claim 1 characterized in that the ester is at least one material selected from the group of glycerol phosphate, glycerol borate, and glycol borate.

4. A composition according to claim 1 characterized in that said ester is a mixture of polyethylene glycol phosphate and at least one ester selected from the group consisting of glycerol phosphate, glycerol borate, and glycol borate.

5. A composition according to claim 3 characterized in that the polyethylene glycol phosphate is at least about one-half of the total ester.

6. A composition to be dissolved in water to provide an aqueous acid bath for applying to ferrous metal stock to form thereon a microporous lubricating film which is chemically bonded to the stock and consisting essentially of the following:

Oxalic acid	About 10 to 30 parts.
Phosphoric acid (about 85% concentration)	About 5 to 15 parts.
Hypophosphorous acid (about 50% concentration)	About 1 part.
and	
Polyethylene glycol phosphate	About 5 to 15 parts.

7. A composition to be dissolved in water to provide an aqueous acid bath for applying to ferrous metal stock to form thereon a microporous lubricating film which is chemically bonded to the stock and consisting essentially of the following:

Oxalic acid	About 25 parts.
Phosphoric acid (about 85% concentration)	About 10 parts.
Hypophosphorous acid (about 50% concentration)	About 1 part.
and	
Polyethylene glycol phosphate	About 10 parts.

8. The method of providing on ferrous metal stock a microporous lubricating film which is chemically bonded thereon and comprising subjecting the stock to a hot aqueous acid bath consisting essentially of about 5 to 15 parts of phosphoric acid, about 1 part of hypophosphorous acid, about 10 to 30 parts of a material selected from the group consisting of oxalic acid, zinc oxalate, and zinc phosphate, and mixtures of the foregoing, and about 5–15 parts of an acid-soluble, aliphatic, polyhydric alcohol ester having less than four hydroxy groups of an inorganic acid, and which is non-reactive to said bath, maintaining the stock subjected to the bath until the desired film is formed, then removing the stock.

9. The method of providing on ferrous metal stock a microporous lubricating film which is chemically bonded thereon and comprising subjecting the stock to a hot aqueous acid bath consisting essentially of about 5 to 15 parts of phosphoric acid, about 1 part of hypophosphorous acid, about 10 to 30 parts of a material selected from the group consisting of oxalic acid, zinc oxalate, and zinc phosphate, and mixtures of the foregoing, and about 5 to 15 parts of an acid-soluble, aliphatic, polyhydric alcohol ester having less than four hydroxy groups of an inorganic acid, and which is non-reactive to said bath, maintaining the stock subjected to the bath until the desired film is formed, then removing the stock and drying the stock at a temperature of from about 400 to 450 degrees Fahrenheit.

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