United States Patent Office 2,876,148 Patented Mar. 3, 1959

2,876,148

COLD WORKING METALS COATED WITH COLLOIDAL SULFUR

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No Drawing. Application October 5, 1954
Serial No. 460,503

15 Claims. (Cl. 148—6.24)

This invention relates to a method of cold working metals. More particularly, the invention relates to cold working or plastic deformation of metal articles in the presence of a sulfidizing agent. The sulfidizing agent forms a sulfide coat or film with the metal on its surface, and the coat prevents the tool from biting into the article in the cold working operation.

This application is a continuation-in-part of my copending application, Serial No. 357,351, filed May 25, 1953, now abandoned, and the disclosure of the latter application is incorporated herein and made a part hereof by reference as fully as if it were set forth herein in its entirety.

In cold working metals, it is necessary to provide an intermediate layer between the metal to be worked and the tool or die, as otherwise, the tool would bite into the metal, resulting in damage to the tool and the metal surface to be worked. Numerous materials have been proposed for this purpose.

It has now been found in accordance with the invention that metals are very advantageously cold worked in the presence of a water-insoluble sulfidizing agent which is capable of reacting with a ferrous surface in the cold and in the presence of water to form a black tightly adherent film of iron sulfide. Specifically, the sulfidizing agent employed is colloidal sulfur. In the cold working operation, the metal is contacted with the colloidal sulfur at its zone or region of deformation.

By chemical reaction between the sulfidizing agent and the metal when the metal is undergoing deformation, a coat or film of metal sulfide forms on the metal, and this coat prevents biting in of the tool. At the same time, a metal sulfide coat forms on the die, by reaction with the metal of the die. These coats not only function as protective layers on the metals, but they also function as lubricants to reduce friction. An accompanying advantage of cold working in the presence of the sulfidizing agent is that the agent itself functions as a lubricant, further reducing friction.

Colloidal sulfur employed as the sulfidizing agent in the invention is a particularly reactive form of sulfur which due to its very small particle size of below .1 micron, ranging between .01 to .1 micron, forms colloidal aqueous solutions and produces a sulfide film on metals in the presence of water even in the cold.

Colloidal sulfur such as is produced by introducing hydrogen sulfide into a cold solution of sulfur dioxide or by decomposing sodium thiosulfate by means of dilute sulfuric acid may be used. In this way, colloidal sulfur is obtained in the form of a 50–60 percent emulsion in water, as a paste, or in form of solid pieces containing 60 to 85% sulfur. Other modifications of colloidal sulfur such as are produced by grinding common sulfur with inert materials like urea, grape sugar, lactose, and fission products of casein, may also be used. It is to be noted that there is no formation of colloidal sulfur when sulfur is ground in the absence of such materials. Apparently, the finely comminuted particles then reaggregate to larger particles. This colloidal sulfur produced by dry methods contains 70 to 80% sulfur, a few percent of water and the balance of the inert by materials which were used in its production.

The process is carried out by applying a composition containing the sulfidizing agent to the metal articles during the mechanical cold working or plastic deformation of the articles. The main fields of application of the present process are in wire, profile and tube drawing, in which concentrates may be employed to advantage.

The invention finds its greatest utility in the working of ferrous and nickelous metals, e. g., iron, steel, nickel and nickel alloys. The sulfidizing agent is ordinarily provided on the metal in the cold, that is, at normal atmospheric temperature. The agent is applied, for example, by brush-coating the dry agent or in the form of a paste, by immersing the article in a bath, by spraying, or by drying a dispersion on the article prior to working. The method of application and the contents of the composition applied varies with the work, the ingredients of the composition and the type of operation. In wire drawing industry, it is a widespread practice to first provide the wire with a lime coating and to then draw the dried lime-coated wire with calcium stearate as a lubricating means. Colloidal sulfur may be used in the same manner by spraying the wire with or dipping it into a suspension or colloidal solution of the sulfidizing agent, allowing it to dry, and then drawing it with the aid of conventional lubricants applied to the surface of the wire. The colloidal sulfur can be used alone in dry powder form, as the sole agent providing the functions of coating and lubrication of the article, in the same manner as the dry lubricants in wire drawing are used, by pulling the article through a container arranged in proximity to the die and filled with the powder. Adhesives may be added, or the articles may be provided with a breath-thin layer of adhesives like glycerine and aqueous solutions of cellulose glycolate.

The reactivity of the colloidal sulfur is enormously increased due to the heat and pressure prevailing in the die hole during the cold working operation, the surfaces of the metal article and the die becoming as hot as 200° C. and more, and there results an instantaneous formation of metal sulfide on the article being worked as well as on the die itself. The fact that a sulfide coating is likewise formed on the working surface of the die permits use of very cheap steels for making the dies instead of the very expensive tungsten carbide.

The reactivity of colloidal sulfur is further increased by the presence of water. However, colloidal sulfur and water are proportioned to provide the die hole temperatures necessary for the reaction and formation of the proper sulfide coat. Thus, as any larger content of water would decrease the reactivity due to its cooling action, in cold working metals and alloys of high sulfur resistance, it is preferred not to use contents of water in the colloidal sulfur larger than about ten percent.

As the reactivity of the colloidal sulfur is to a high degree dependent upon the temperature, starting the operation with cold tools would result in an inadequate formation of the sulfide film until the working temperature of the die has been reached. A preferred method involves heating the die at the start or after interruptions of operation to about 50–100° C.

In the practice of the invention, sulfidizing compositions having a relatively low content of colloidal sulfur provide successful working of metals such as low carbon steels which are highly reactive in forming metal sulfides. However, for cold working metals of high sulfur resistance such as steels of higher carbon and/or alloy content, higher percentages of sulfur are preferred;

that is, compositions having greater than about 40% by weight of colloidal sulfur are preferred for such resistant steels and alloys, for successful working. It is further preferred to use a composition containing greater than about 60% of colloidal sulfur for the most resistant metals.

When the colloidal sulfur is produced by wet methods and contains more water than is desired and particularly, when it is desired to provide a composition having a very high sulfur content on the metal, such compositions may advantageously be used by dipping the work pieces into the aqueous suspension of the colloidal sulfur to provide a film of the suspension on the articles, allowing the suspension adhering to the work piece to dry in the open air, and cold working the work pieces thus provided with a film of residual moisture-containing colloidal sulfur with or without the application of conventional lubricants or other assistants. Desiccation of the suspensions prior to application would require precautionary measures to avoid the formation of crystalline sulfur.

When an article is coated with colloidal sulfur before the cold working, the sulfur is sufficiently reactive to produce a sulfide film on the article. Also, the sufidizing agent is a lubricant. However, the article is not protected thereby sufficiently for the working, and the proper formation of a sulfide coating which will serve the intended purpose takes place in the region of the die at the elevated temperatures prevailing there, where the metal surface contacts the die.

In order to reduce friction of the work in the die and the hardening effect of cold working, additions of conventional lubricants of any type used in cold working metals may be made. Preferred conventional metal working lubricants are long chain fatty alcohol sulfonates and water-insoluble soaps, for example, calcium or aluminum stearates, and oil-in-water emulsions. Less advisable is the use of mineral and vegetable oils and water-in-oil emulsions, as oils have a tendency to dissolve colloidal sulfur. Sulfur dissolved in organic solvents is practically ineffective.

Other lubricants suitable for use with the sufidizing agent are described in the above application. A conventional lubricant may be included in one lubricating composition with the colloidal sulfur, or the two may be applied separately. Thus, the article may be provided with a coating of colloidal sulfur, and then the cold working may proceed in the further presence of the lubricant.

The amounts of the ingredients of the sulfidizing agent compositions according to the invention depend on the reactivity of the metal to be worked to form metal sulfide. Low carbon steel, for instance Armco iron, the reactivity of which in contact with sulfidizing agents is extremely high, can be successfully worked with mixtures of:

10 to 20% of aqueous colloidal sulfur, prepared as described above, containing 50 to 60% colloidal sulfur, the balance being water, and
90 to 80% of a cutting oil emulsion containing about 50% of cutting oil and 50% of water, the cutting oil being composed, for example, of about 86% of a mineral oil and about 14% of an emulsifier.

The above and the other proportions given in the specification are by weight.

For cold working steels of up to 0.25% carbon content, the following mixture can be employed:

40 to 30% of aqueous colloidal sulfur containing 50 to 60% sulfur and the balance of water, and
60 to 70% of the above cutting oil emulsion.

In cold working less reactive metals, for instance, steels of higher carbon and/or alloy content, higher percentages of sulfidizing agent in the mixtures are preferred, for example, as in mixtures which are composed of:

60 to 90% of colloidal sulfur containing 70 to 80% sulfur and 3% water, the balance being inert material added to crystalline sulfur, when ground to colloidal sulfur, and
40 to 10% of calcium stearate containing 3% water.

Another exemplary mixture consists of:

80 to 90% of aqueous colloidal sulfur containing 50 to 60% sulfur, and
20 to 10% of ammonium dodecyl benzolsulfonate.

Preferred high-sulfur compositions, for very resistant metals, are, for example:

90% of colloidal sulfur containing 70 to 80% sulfur and up to 10% water, the remainder being inert materials, and
10% of calcium stearate containing 3% water;

and

80 to 90% of colloidal sulfur containing 85% sulfur, the remainder being up to 10% water and protective colloids,
20 to 10% ammonium dodecylbenzolsulfonate.

Colloidal sulfur may be used alone, without the addition of conventional lubricants, either in aqueous suspension, in aqueous pastes or as a powder, depending on the reactivity of the metal, the reduction rate and the moldability of the metal.

In applying the colloidal sulfur in the aforesaid manner, additions of wetting agents such as fatty alcohol sulfonates (which can also be employed as lubricants, as described above) and adhesive agents such as cellulose glycolate to the aqueous suspensions of the colloidal sulfur may advantageously be used in order to ensure a uniform wetting of the metal surface, a uniform distribution of the colloidal sulfur on and the necessary adhesion thereof to the metal surface.

In such an application of the colloidal sulfur, 2 parts by weight of cellulose methyl ether or cellulose glycolate may be dissolved in 96 parts by weight of an aqueous suspension of colloidal sulfur containing about 30 to 40% sulfur and the balance of water. To this mixture, 2 parts by weight of dodecylbenzolsulfonate are added and dissolved. The articles to be cold worked are dipped into this mixture and then allowed to drain and dry in the open air. As soon as the articles are visibly dry, they are cold worked.

It has been proposed previously to use a wire drawing lubricant consisting of a dry mixture of flowers of sulfur and wire drawing soap. However, flowers of sulfur, which are crystalline even if finely comminuted, are not capable of chemically reacting with iron surfaces in a dry state at normal temperatures and only form a barely visible, ineffective film of iron sulfide in the presence of water, possibly due to the sulfur dioxide content. On the other hand, humid colloidal sulfur as employed in the invention is characterized by forming a black tightly adherent sulfide film with a ferrous surface when in contact therewith at normal atmospheric temperature. The action of the flowers of sulfur in the prior process is merely a physical one, while in the present process the colloidal sulfur reacts chemically with a ferrous surface to form a substantial and effective iron sulfide coating.

The sulfide coat or film produced according to the invention, although thin, has proved to be very effective in facilitating the cold plastic deformation of metals and to prevent the tool from biting into the metal being worked. The present method is to be distinguished from the production of a sulfide coat in a separate operation preceding the metal working. The invention obviates the separate production of a sulfide coat by combining the coating and cold working in one operation. Where

the colloidal sulfur is continuously provided in contact with the metal article, there is the advantage that if the coating is damaged by the tool, it is immediately and continuously renewed. Thus, the invention has important advantages over prior methods and provides a very simple and economical process.

Colloidal sulfur, which is water-insoluble, provides certain advantages over the water-soluble sulfidizing agents. It is odorless and not poisonous. Water-soluble agents such as ammonium sulfide require the presence of oxygen for formation of the metal sulfide, according to the equation, $H_2S+Fe+O \rightarrow FeS+H_2O$.

The invention is hereby claimed as follows:

1. In a method of cold working a metal article, the step which comprises contacting the metallic surface of the article with colloidal sulfur having a particle size below about .1 micron and a water content of not less than about 3% by weight when it is being deformed and at its zone of deformation, thereby forming a protective coat of metal sulfide on the article.

2. A method according to claim 1 in which the water content of said colloidal sulfur is a maximum of about 10% by weight.

3. A method according to claim 1 in which said colloidal sulfur is present in a composition containing greater than about 60% by weight of colloidal sulfur.

4. A method according to claim 1 in which said colloidal sulfur is the sole agent providing coating and lubrication of the article.

5. A method according to claim 1 in which the tools are heated at the start of operation.

6. In a method of cold working a metal article, the steps which comprise providing the metallic surface of the article with a film of an aqueous suspension of colloidal sulfur having a particle size below about .1 micron, allowing the film to dry in the atmosphere, and cold working the thus coated article.

7. In a method of cold working a metal article, the step which comprises contacting the metallic surface of the article with an aqueous composition containing colloidal sulfur having a particle size below about .1 micron when it is being deformed and at its zone of deformation, thereby forming a protective coat of metal sulfide on the article, said composition also containing a water-insoluble soap lubricant.

8. In a method of cold working a metal article the step which comprises contacting the metallic surface of the article with an aqueous composition containing colloidal sulfur having a particle size below about .1 micron when it is being deformed and at its zone of deformation, thereby forming a protective coat of metal sulfide on the article, the sulfur and water in said composition being proportioned to provide die hole temperatures suitable for the formation of said coat.

9. In a method of cold working a metal article, the steps which comprise providing the metallic surface of the article with a film of an aqueous suspension of colloidal sulfur having a particle size below about .1 micron and containing a wetting agent and an adhesive agent, allowing the film to dry in the atmosphere, and cold working the thus coated article.

10. The method of claim 1 further defined in that said colloidal sulfur is used in a mixture with conventional metal working lubricants.

11. The method of claim 1 further defined in that said colloidal sulfur has a particle size ranging between .01 to .1 micron.

12. A method of cold working a metal article comprising the steps of contacting said metal article with colloidal sulfur having a particle size below about .1 micron and a water content of not less than about 3% by weight and plastically deforming said coated article.

13. A method of cold working a metal article comprising the steps of contacting the surface of said article with an aqueous composition of colloidal sulfur having a particle size below about .1 micron thereby forming a metal sulfide coating on said article, and cold working said coated metal article.

14. In a method of cold working a metal article, the step which comprises contacting the metallic surface of the article with colloidal sulfur having a particle size below about .1 micron and a water content of not less than about 3% by weight.

15. In a method of cold working a metal article, the step which comprises contacting the metallic surface of the article while the article is being worked with colloidal sulfur and a lubricant, said colloidal sulfur having a particle size below about .1 micron and a water content of not less than about 3%.

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