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METALLIZED PRODUCT AND PROCESS FOR PREPARING THE SAME

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Fig. 1.

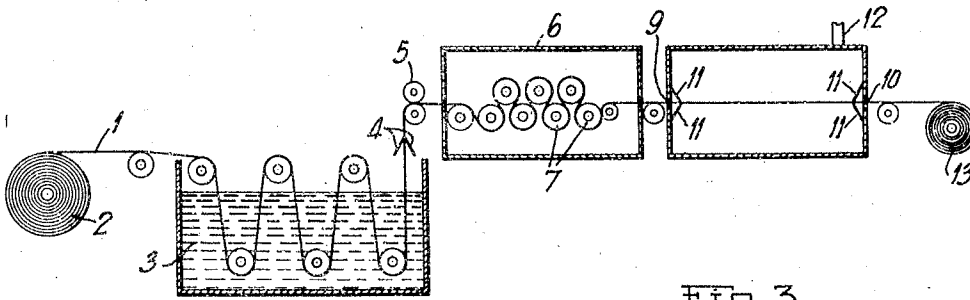


Fig. 2.

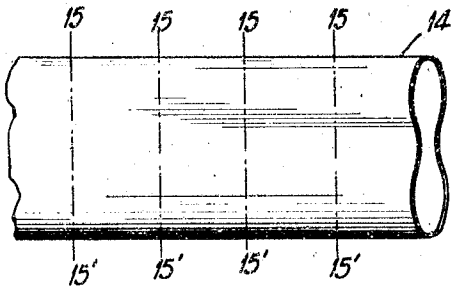


Fig. 3.

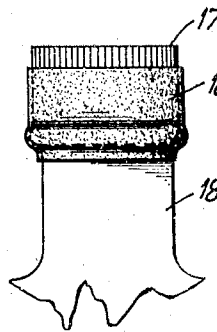


Fig. 4.

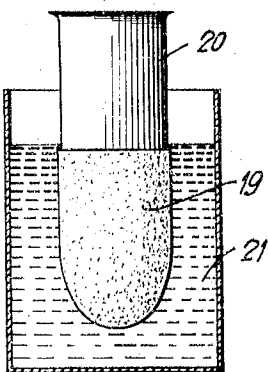
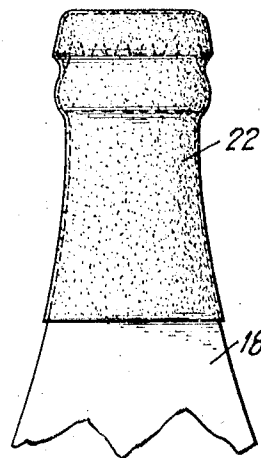


Fig. 5.



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# UNITED STATES PATENT OFFICE

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## METALLIZED PRODUCT AND PROCESS FOR PREPARING THE SAME

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11 Claims. (Cl. 91—68)

The invention relates to a process for imparting a metallic appearance to material. More particularly, it relates to a process for producing a coating having a metallic appearance on non-fibrous, non-porous, flexible, organic materials and to articles produced thereby, and includes correlated improvements and discoveries whereby the production and the character and qualities of such materials are enhanced.

Heretofore in imparting a metallic effect to sheets, films and other articles by chemical processes, it has been customary to pass the article first through a solution designed to deposit upon the surface one of the reagents required, e. g., silver nitrate, and thereafter to treat the article with a solution of the other reagent, e. g. sodium sulphide, which reacts with the first reagent to produce on the surface a deposit of metal sulphide having a metallic appearance.

It has been found, however, that when the second solution is applied, the reaction takes place chiefly only on the surface of the material, and the precipitate which is formed adheres only imperfectly thereto. Moreover, the sulphide is not uniformly deposited from the solution by reason of the fact that no matter how carefully the second solution is applied, the liquid appears to flow across the surface and the deposit is laid down more heavily at the edges of the stream so as to produce ripples in the coating. Such prior coatings are characterized by having little adherence so that they may be wiped off easily, by showing a very uneven reflectivity and by exhibiting interference colors which detract from the metallic appearance.

It is an object of the invention to overcome the disadvantages of the prior practice and to produce a uniform and strongly adherent coating having a metallic appearance on sheets, films, hollow bodies and articles formed in desired manners and shapes from a non-fibrous material.

It is another object of the invention to provide an improved process for producing a coating on various materials which simulates a metal surface of high lustre.

A further object of the invention is to provide, as a new article of manufacture, sheets or films having a coating thereon which is extremely thin, uniform, flexible and of high metallic lustre, and which is strongly adherent to the base.

It is a specific object of the invention to provide hollow bodies, such as shrinkable container closures, having a coating thereon simulating in appearance a metallic surface of high lustre.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

In the practice of the invention a film base, e. g. a sheet, film, hollow body, molded object,

etc., formed of a non-fibrous material carrying a heavy metal salt is contacted with a sulphur compound in gaseous phase whereby an insoluble sulphide is formed. This may be effected by treating the non-fibrous material with a solution of a heavy metal salt, and subsequently drying the surface of the material, whereby the material is impregnated with the salt, and then exposing to the action of a sulphide in a gaseous state, whereby there is formed substantially on the surface of the article a strongly adherent, uniform and flexible coating of metal sulphide having a metallic lustre.

The invention accordingly comprises a process having the steps and the relation of steps one to another, and an article having the features, properties and elements all as described in the following detailed description and the scope of the application of which will be indicated in the claims.

For a more complete understanding of the nature and objects of the invention, reference should be had to the attached drawing in which:

Fig. 1 depicts a diagrammatic representation of a suitable procedure for carrying out an illustrative embodiment of the invention as employed in the manufacture of sheets and films having a metallic effect;

Fig. 2 is a section of a seamless tubing metallized in accordance with the process of the invention;

Fig. 3 is a representation of a closure band formed from the tubing of Fig. 2;

Fig. 4 is a view partly in section of a means of forming hollow bodies which are then metallized, and

Fig. 5 is a representation of a shrinkable closure cap formed according to that modification of the process illustrated in Fig. 4.

The process is applicable for treating various types of non-fibrous, non-porous, flexible, organic materials, for example, a regenerated cellulose, an alkali-soluble cellulose ether such as diethyl cellulose, an alkali-insoluble cellulose ether, cellulose esters, as cellulose nitrate and cellulose acetate, an alkali-soluble oxy-ether of cellulose, gelatin, casein, synthetic resins. Also, a high gloss paper, as glassine, may be used. When treated, the materials may be in the form of a sheet, a film, endless tubing, a band, a ribbon, a filament, a hollow body and articles of desired size and shape formed from any material or combination of the materials above mentioned.

It has been found desirable in producing a coating having a marked resemblance to a metal surface to employ a base material which is opaque and/or colored, and preferably one which is also black, although novel and interesting effects can be obtained by the use of opaque and

transparent materials of various colors such as dark blue, red, yellow, green.

Referring to Fig. 1, a sheet 1 of the non-fibrous material is passed from a roll 2 through a solution 3 containing a small quantity of a heavy metal salt, for example, silver nitrate, the solution being contained in a suitable vat. From the bath, the sheet 1 passes next through a pair of doctor blades 4 which remove the excess surface liquid and then through a pair of spreading rollers 5 which smooth out any wrinkles which may be produced in the sheet by the action of the salt solution. The sheet passes now into a suitable drying apparatus designated generally as 6 wherein the surface of the sheet is dried as it passes over a plurality of heated rolls 7.

The dried sheet is then passed through an atmosphere containing a sulphide in the gaseous state. For example, the sheet may be passed through a chamber 8 containing hydrogen sulphide gas and having an entrance slit 9 and an exit slit 10, the slits being closed to the escape of the gas by suitable flexible valve flaps 11 positioned to contact the entire surface area of the sheet. If desired, the gas may be circulated through the chamber, but since the amount required is small, it will suffice usually to provide only for renewing the supply of gas through a suitable valve 12. Silver sulphide is formed by the reaction of the hydrogen sulphide gas with the silver nitrate, with which silver sulphide the surface of the sheet is impregnated. From the chamber 8, the sheet passes to the wind-up roll 13. If necessary, the material may be further dried after undergoing the metallizing treatment.

In a similar manner, the process may be carried out for the production of a metallic coating on a hollow body, or a molded article formed, for example, of an opaque, non-fibrous, homogeneous material. Thus, a shrinkable container closure in the form of a narrow band may be given a metallic lustre by passing a section of a seamless, flexible tubing through the apparatus shown in Fig. 1 substantially in the manner as in the treatment of sheet material. As shown in Fig. 2, the metallized tubing 14 is then severed at intervals transverse of the web along the lines 15-15' into suitable bands which may be preserved until use in a suitable preservative.

As illustrated in Fig. 3, the finished band 16 may be placed over a cap of the screw type 17 of a bottle 18 and allowed to shrink thereon in a known manner. After shrinking through drying, the dried band has a beautiful metallic lustre which greatly enhances the appearance of the closure.

For producing metallic coatings on hollow bodies, such as shrinkable container closures in the form of caps, a plurality of caps 19 may be supported on suitable mandrels 20, dipped into the bath 21 of silver nitrate as shown in Fig. 4, and the surface dried by suitable means. The mandrels holding the treated caps are now placed in a chamber containing hydrogen sulphide gas. After sufficient treatment, the gas may be exhausted from the chamber and the caps removed and placed in a suitable preserving liquid until ready for use. The finished cap 22, as illustrated in Fig. 5, may be placed over the mouth and neck of a bottle 18 so as to cover completely the mouth portion of the container.

For the heavy metal salt, there may be employed soluble salts of silver, lead, bismuth, mercury, gold, platinum, copper, iron, chromium, nickel, cobalt, tin and the like, such as the ni-

trates, chlorides, sulphates of these metals. The solution preferably is very dilute. For example, it may comprise from 0.05% to 1% of the desired salt in a suitable solvent. The solvent for the salt may comprise a liquid which is non-solvent of the base material to be coated and a liquid which is a wetting agent therefor, or which has a tendency to wet, swell and/or render tacky the surface of the material. Thus, in metallizing regenerated cellulose, the solvent may contain about 65-70% ethyl alcohol and the remainder water; for metallizing a cellulose derivative, for example, cellulose acetate soluble in alcohol and other organic solvents, the solvent consists of water and a substance which wets the surface of the cellulose derivative, as acetone. In treating articles which have been softened or plasticized with glycerine, a solvent such as alcohol is preferred as it does not remove glycerine from the material. However, the invention also contemplates the use of metal salt solutions containing a quantity of glycerine sufficient to maintain the desired content of glycerine in the material.

The time of immersion of the article in the solution is short, preferably on the order of one minute for a solution having a concentration of from 0.05% to 0.1% of silver nitrate. By varying the concentration of the salt in the solution, the amount of the insoluble sulphide may be varied and thereby the color and depth of the metallic lustre may be altered to suit the purpose for which the article is to be used. Even with the heavy amount of the salt on or in the surface of the article, the action of the gaseous sulphide results in a uniform coating, although care must be taken that the surface is dry after the excess of the solution remaining on the sheet is evenly distributed. If a modified tone or shading is desired, the metal salts may be utilized in compatible admixtures, and such admixtures may contain a salt of a metal, which forms a colored sulphide as cadmium and antimony, in an amount of 10% to 25%.

The sulphide employed may comprise any compound containing sulphur which is capable of volatilization and which reacts with a metal salt to give a binary metal sulphide. For example, the sulphide may be a hydrogen sulphide, an ammonium sulphide, an organic sulphide, as mono- and di-methyl and ethyl sulphides, and other compounds containing loosely combined sulphur. Where an acid is produced by the reaction of the salt and sulphur compound, a small amount of ammonia gas may be added to the gaseous sulphur compound to neutralize the acid.

If it is desired to increase the adherence of the metallic coating, the metal sulphide deposit may be covered with a transparent composition, such as a lacquer containing a cellulose ester and a plasticizer. This is particularly advantageous where the article is in the form of sheet material; is designed for use as a wrapping material, and will be subjected to handling and abrasion. The coating may comprise a moistureproofing ingredient, for example, wax adapted to render the article resistant to the diffusion of water vapor and, further, it may be colored, if desired, to enhance the appearance of the metallic surface.

The foregoing procedures produce a uniform, flexible coating which is highly reflecting and has a metallic lustre. When examined under the microscope, the coating appears to be discontinuous. Further, the coating has a glossy appearance and high lustre only if the article

has a relatively smooth and glossy surface. If the article has a surface which is relatively rough, or if the article is white, the metallic sulphide deposit has a dull metallic lustre instead of a shiny metallic lustre. The coatings produced are strongly adherent by reason of the fact that the salt solutions are such that they penetrate somewhat into the surface of the material so that the metallic sulphide is deposited on and within the surface of the material which results in the coating being strongly bound to the surface.

Since certain changes in carrying out the above process and certain modifications in the article which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

1. As an article of manufacture a film base of non-fibrous, non-porous, flexible, organic material having a strongly adherent coating of a metal sulfide, the exposed surface of said coating being uniform and having a uniform metallic lustre, said coating being produced by treating said material with a solution of a heavy salt, and thereafter subjecting treated material to the action of a sulfur containing gas.

2. As an article of manufacture a colored opaque film base of non-fibrous, non-porous, flexible, organic material having a strongly adherent coating of a metal sulfide, the exposed surface of said coating being uniform and having a uniform metallic lustre, said coating being produced by treating said material with a solution of a heavy salt, and thereafter subjecting treated material to the action of a sulfur containing gas.

3. As an article of manufacture a shrinkable container closure formed from a non-fibrous, non-porous, flexible, organic material having a strongly adherent coating of a metal sulfide, the exposed surface of said coating being uniform and having a uniform metallic lustre, said coating being produced by treating said material with a solution of a heavy salt, and thereafter subjecting treated material to the action of a sulfur containing gas.

4. As an article of manufacture a sheet of regenerated cellulose having a strongly adherent coating of a metal sulfide, the exposed surface of said coating being uniform and having a uniform metallic lustre, said coating being produced by treating said material with a solution of a heavy salt, and thereafter subjecting treated material to the action of a sulfur containing gas.

5. As an article of manufacture a shrinkable container closure formed from regenerated cellulose having a strongly adherent coating of a metal sulfide, the exposed surface of said coating being uniform and having a uniform metallic lustre, said coating being produced by treating said material with a solution of a heavy salt, and

thereafter subjecting treated material to the action of a sulfur containing gas.

6. As an article of manufacture a film base of a material selected from the group consisting of regenerated cellulose, a cellulose ether, a cellulose ester, an alkali soluble oxy-ether of cellulose, gelatine, casein, glassine and synthetic resins having a strongly adherent coating of a metal sulfide, the exposed surface of said coating being uniform and having a uniform metallic lustre, said coating being produced by treating said material with a solution of a heavy salt, and thereafter subjecting treated material to the action of a sulfur containing gas.

7. A process for the manufacture of an article having a metallic lustre, which comprises treating a film base of non-fibrous, non-porous, flexible, organic material with a solution of a heavy metal salt, and thereafter subjecting the treated material to the action of a sulfur containing gas whereby said material is provided with a strongly adherent coating of a metallic sulfide, the exposed surface of said coating being uniform and having a uniform metallic lustre.

8. A process for the manufacture of an article having a metallic lustre, which comprises treating a film base of non-fibrous, non-porous, flexible, cellulosic material with a solution of a heavy salt in a solvent containing a liquid which is a wetting agent for the material being treated, and thereafter subjecting the treated material to the action of a sulfur containing gas whereby said material is provided with a strongly adherent coating of a metallic sulfide, the exposed surface of said coating being uniform and having a uniform metallic lustre.

9. A process for the manufacture of an article having a metallic lustre, which comprises treating regenerated cellulose with a solution of a heavy metal salt in a solvent containing a liquid which is a wetting agent for the regenerated cellulose, drying the surface of the treated cellulose, and thereafter subjecting the treated material to the action of a sulfur containing gas whereby said material is provided with a strongly adherent coating of a metallic sulfide, the exposed surface of said coating being uniform and having a uniform metallic lustre.

10. A process for the manufacture of an article having a metallic lustre, which comprises treating opaque regenerated cellulose with a solution of a heavy metal salt in a solvent comprising a mixture of a liquid which tends to soften the surface of the regenerated cellulose and a liquid which is a non-solvent therefor, drying the surface of the thus treated cellulose, and thereafter subjecting the treated material to the action of a sulfur containing gas whereby said material is provided with a strongly adherent coating of a metallic sulfide, the exposed surface of said coating being uniform and having a uniform metallic lustre.

11. A process for the manufacture of pellicles having a metallic lustre, which comprises treating a pre-dried, flexible pellicle of non-fibrous, non-porous organic material having a coating of a metallic salt thereon with a sulfur containing gas whereby the material is provided with a strongly adherent coating of a metallic sulfide, the exposed surface of said coating being uniform and having a uniform metallic lustre.

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