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COATING

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This invention relates to coatings and more particularly to moistureproof coatings for sheet materials and the like.

Most coatings of this type are applied by dissolving the composition in a volatile solvent, applying the solution to the material, and heating the material to drive off the solvent. This process is necessarily expensive to carry out since either the solvent must be lost, or a cumbersome and expensive apparatus must be arranged to collect it upon evaporation. Also when the coating is applied to a printed surface the solvent will often dissolve a portion of the ink and cause "bleeding" and when the material to be coated is porous, the volatile solvent will cause the coating to penetrate the surface to an undesirable extent. And more important, the speed of the coating process is limited to the speed at which the coating may be dried. For instance, in coating sheets of paper the sheets cannot be laid upon each other and hence are difficult to dispose of until the coating has dried. In the case of printing, many complicated methods have been worked out to prevent this offset but they are expensive and unsatisfactory at best.

I have found that these difficulties are obviated by the use of a solvent which becomes a permanent constituent of the coating. In other words, apply a molten solution of normally solid substances to the material coated which may then be cooled to immediately solidify the coating.

Various types of coatings have previously been applied in the molten state. Coating with molten wax, for instance, is quite common. Similarly, water insoluble soaps have been applied in the molten state. These coatings, however, do not satisfactorily perform the functions of the coatings which may be applied by means of the use of a volatile solvent.

I have found that by a proper choice and mixture of suitable ingredients, solid solutions of coatings may be prepared which have all of the desirable properties of coatings applied with volatile solvents and yet retain the advantages attendant upon molten application. Still other properties are obtained which are entirely novel in themselves.

My novel mixture contains two essential ingredients, a water-insoluble soap and a resin in solid solution in each other or in another substance. Preferably, each ingredient acts as a solvent for the other and no other substances need be added to prepare the solution.

Relatively small amounts of certain other substances such as plasticizers, for instance, may

be added and the proportions of the essential ingredients may be varied depending upon the type of coating desired and the purpose for which it is to be used.

Water-insoluble soaps have been used alone as coatings but have never been satisfactory because of their poor qualities of adherence. Unless the material to be coated is porous a soap alone will not adhere to it. And even if the material is porous the soap will adhere only upon penetration of the surface which increases the cost and gives a less desirable coating. On the other hand, a resin coating alone fails to give adequate protection against moisture. Also, if the resin has a relatively low melting point, the coating will become tacky on warm days while if it has a high melting point, it is impractical to apply it in the molten state without driving the moisture out of the material to be coated which causes blistering of the coating and weakens the material if it consists of organic fibers.

By the use of a solid solution containing both a resin and a water-insoluble soap a moisture proof coating is obtained which adheres firmly to the material to be coated. Also, the mixture, since a solution is formed, has a lower melting point than that of either of the constituents. Hence substances having melting points so high that their molten application would drive the moisture out of the material to be coated may be applied in this manner. Also, the solution will not become "tacky" or tend to flow at a temperature as far below its melting point as will the resin alone.

Various other features of my invention add other desirable properties to the coating. Normally as the coating solidifies, the soap, being a salt, will crystallize; so also will certain resins. As a result the coating will be opaque. If, however, the solution after application is quickly chilled to a temperature below the melting point, it will solidify to form a translucent glossy coating. Such a coating makes an attractive appearance, allows printing to be visible through the coating, does not stick to other surfaces, and is more resistant to scuffing and chafing. Unless the constituents are united in the form of a solid solution, however, the coating will be dull or even opaque. For instance, if a polymerized, insoluble resin is used or if the coating is baked to polymerize the resin an opaque coating will be formed.

The time and temperature relations are important in obtaining a desirable coating. If a temperature greatly above 212° F. is used the solution must be cooled very quickly after appli-

cation in order to prevent vaporization of the moisture and the resulting blistering of the coating and weakening of the material. For instance, to use a solution melting above 250° F. a coating apparatus must be used which will chill the solution very rapidly, preferably in from two to four seconds. On the other hand, if a solution is used which has a melting point below or only slightly above 212° F. it is not necessary to chill the coating so quickly, ten seconds or more being sufficiently rapid. But to secure a satisfactory coating the solution must be such that it will not soften or become tacky at temperatures below 135° F.

Thus it will be seen that, other factors being equal, a coating with a low but sharp melting point is desirable. I have found that such may be obtained by using various mixtures of soaps and resins.

For the ingredient of a water insoluble soap, I prefer to use one or a mixture of the stearates, palmitates, abietates, linoleates, or oleates of the heavy metals, preferably one of the group including zinc, cadmium, tin, magnesium, aluminum, antimony, bismuth, and lead. The soaps of most of the lighter metals especially those of the alkali metals, are too soluble in water to be used, as the resistance of the coating to moisture depends in a large measure upon the insolubility of the soap ingredient in water. Some of the soaps mentioned, for instance, those containing a high percentage of zinc stearate are not only moisture proof but are insoluble in the more common organic fats, oils, and hydrocarbons as well.

Another group of water-insoluble soaps, which may be used, consists of the soaps formed by the above mentioned heavy metals with a natural wax such as Japan wax, myrtal, carnauba wax or candillila wax or with a natural resin such as dammar, elemi or a copal resin. Usually zinc or magnesium is used as the metal constituent of these soaps.

Certain soaps which have particularly desirable moisture proofing and oil resisting properties such as the stearates of zinc, magnesium and lead, have relatively high melting points and as a result their use is greatly limited in the absence of a means of lowering the melting points.

I have found that by using a proper combination of soaps an eutectic mixture is obtained and considerable lowering of the melting points results. This eutectic mixture has characteristics analogous to those of metals and those of non-polar compounds but may not be predicted from the eutectics of the metals or of the organic radicals present in the soaps. For instance, a mixture of the stearates of zinc and magnesium forms an eutectic when the composition of zinc stearate is sixty percent. It is believed that when a temperature composition curve of a salt is graphically plotted for a given mixture it may be used to predict the eutectic of the same salt in a new mixture.

Another factor of great importance is the fluidity of the coating composition, or in other words, its free-flowing characteristics in the molten state. This depends upon the viscosity, the surface tension and other properties. The more free-flowing the solution is, the lower is the temperature at which it may be applied. This is a particularly valuable property when the solution is being used as a solvent for a printing ink, in which case a high degree of fluidity at a relatively low temperature is essential.

I have found that the manner in which a mixture of soaps is prepared determines, to a large extent, the viscosity of the molten mixture. For instance, a mixture of the stearates of zinc and magnesium has a lower viscosity over a wider range of temperatures when prepared by reacting stearic acid first with magnesium oxide and then with zinc oxide than when the stearic acid is reacted with the zinc oxide first or when the two prepared stearates are mixed. The same is true of a mixture of the stearates of lead and magnesium when the stearic acid is first partially neutralized with magnesium oxide and then the balance of the acid neutralized with basic lead carbonate. These unusual properties may possibly be due to a double salt formation, an inter-compound formation, a secondary valence combination or to a particularly crystalline structure in the solid state. At any rate, for the purpose of simplicity, I shall describe it merely as a mixture.

The composition of the mixture will, of course, also affect the viscosity. Thus in determining the composition desired both the viscosity and the melting point must be considered. Once the most favorable composition for the particular properties desired has been determined, then it remains only to prepare the mixture in such a manner as to obtain the lowest viscosity.

For the second essential ingredient, the resin, any of a large number of substances, may be used. The resin must, however, be soluble rather than polymerized, insoluble, and infusible. Otherwise it will not dissolve in the solvent used. Preferably, the resin should be soluble in the soap used, thus eliminating the necessity of another solvent. Among the suitable commercial resins are modified ester resins such as "Rauzene 4CR" and "Rauzene 88B" sold by the Robert Rauh Company, chlorinated diphenyls such as "Aroclor 5460" sold by the Monsanto Chemical Co. and "Nevillite" made by Neville Co. Also natural resins such as dammar and elemi may be used.

It is usually desirable to mix two or more resins since ordinarily no one resin will have all of the properties such as melting point, viscosity, adhesive qualities, and solubility which may be desired for a particular purpose.

For many purposes it is desirable, although not necessary, to use a small quantity of a plasticizer such as a liquid resin or a wax in the coating composition. This imparts greater flexibility to the mixture and decreases its friability. Among the commercial resins which may be used as plasticizers is a low melting chlorinated diphenyl "Aroclor 1254" made by the Monsanto Chemical Co. Paraffin wax may also be used.

Other properties may be imparted to the coating by adding relatively small proportions of various ingredients. The toughness of the coating may be increased by adding a cellulose compound that is thermoplastic, for example, ethyl cellulose, to the mixture. In order for the composition to be compatible with the ethyl cellulose I have found that the acid form of the stearate should be used. For example, I use a coating mixture of the following composition:

	Parts
50% magnesium acid stearate.....	55
Resin.....	25
Ethyl cellulose.....	15
A plasticizer.....	5

The plasticizer used should be of a type par-

ticularly adapted for cellulose compounds such as butyl phthalyl butyl glycolate, sold under the trade name of "Santicizer," are well suited for this purpose. Sulfonamides and sulfonates such as ortho-cresyl para-toluene sulfonate may also be used.

I have found my coating composition to be especially useful as a printing fluid. In printing it is necessary to have a pigment, a solvent for the pigment and a vehicle to retain the pigment on the paper. In commercial gravure printing, for instance, it is ordinarily considered necessary to have approximately eighty percent solvent in the fluid in order that its fluidity will be great enough to accomplish complete coverage of the printing roll. On the other hand, the pigment must approach twenty percent in order that the paper may be properly colored. Thus when a volatile solvent is used, it is difficult to use sufficient vehicle to hold the pigment on the paper. For this reason, gilsonite which will act as both a pigment and a vehicle is often used even though only one color, brown, may then be printed.

I have found that by using a molten solvent, consisting of a resin and a water-insoluble soap, these difficulties may be obviated. The solvent being a permanent constituent of the coating acts as a vehicle as well as a solvent. Such a composition will easily carry twenty percent or more of a coloring material.

A more important advantage of my invention lies in the speed with which printing may be done. Since the resin-soap solution can be solidified in two to four seconds or even less, anti-offset devices and processes are eliminated entirely and in addition the printing may be done much more rapidly than has heretofore been possible. Where previously the speed of printing has been limited by the rapidity with which the paper could be removed and still prevent offsetting, with the aid of my invention it is limited only by the speed of the printing press. This feature is particularly useful in typographical printing as well as gravure printing and other types.

In addition a more satisfactory product is obtained since it is moisture proof and glossy.

It is possible to use any pigment which has heretofore been used in the printing process. However, when the fluid is to be used in a gravure printing process, I prefer to use a thermoplastic pigment which tends to increase the fluidity of the molten solution. In general, it is desirable but not essential (unless a glossy translucent coating is desired) to use a pigment which is soluble in the resin-soap solution.

Among the coloring materials which have been found to be particularly satisfactory and which are commercially available are: oil soluble bases

"National Oil Red 'O' "
"National Oil Black"

and resin colors

"National Resin Green"
"National Nubian Resin Black"

and "Nigrosene," a thermoplastic oil-soluble coloring material, all made by the National Aniline and Chemical Co.

In the preparation of the printing fluid, a suitable amount of coloring material is added to the resin-soap composition and the mixture melted. The molten solution may then be applied in the same manner as are ordinary print-

ing inks although, of course, the fluid must be maintained at a temperature sufficiently high to keep it in the liquid state.

For the purpose of making the invention clear the following specific examples of my compositions and their application may be set out in detail.

(1) Coating composition

	Per cent
A mixture of forty parts of magnesium stearate and sixty parts of lead stearate prepared by neutralizing stearic acid successively with a magnesium alkali and a lead alkali.....	67.25
Rauzene 4 C. R.....	16.00
Aroclor 1254.....	1.75
Aroclor 5460.....	8.00
Paraffin.....	7.00

The ingredients are mixed, heated to 220° F. to form a molten solution, and maintained at this temperature. The liquid may then be applied to the article to be coated by any of the well known methods for coating with liquids. The coated materials may be chilled by an air blast or in any other manner.

(2) Printing fluid composition

	Parts
A mixture of 50 parts of magnesium stearate and 50 parts of lead stearate prepared by neutralizing stearic acid successively with a magnesium alkali and a lead alkali.....	67.25
Rauzene 4 C. R.....	16
Aroclor 1254.....	1.75
Aroclor 5460.....	8
Nigrosene.....	10

The ingredients are mixed and heated to form a molten solution as in Example 1. The molten solution may then be applied with a printing press as would the ordinary liquid ink, the temperature of the fluid being maintained at approximately 220° F. throughout the operation of the process.

This application is a continuation in part of application Serial No. 47,004, filed October 28, 1935.

The foregoing description has been given for clearness of understanding only and no unnecessary limitations should be understood therefrom but the appended claims should be construed as broadly as permissible in view of the prior art.

I claim:

1. A sheet material containing organic fibers, said fibers having therein a normal amount of moisture, said sheet material having a translucent, glossy, moisture proof coating adhering firmly to said sheet material without appreciable penetration thereof and comprising an eutectic mixture of soaps of at least two of the metals of the group consisting of zinc and cadmium and tin and magnesium and aluminum and antimony and bismuth and lead and a resin soluble in said soaps, said resin and said soaps being in solid solution in each other.

2. A sheet material containing organic fibers, said fibers having therein a normal amount of moisture, said sheet material having a translucent, glossy, moisture proof coating adhering firmly to said sheet material without appreciable penetration thereof and comprising an eutectic mixture of soaps of at least two stearates of metals of the group consisting of zinc and cadmium and tin and magnesium and aluminum

and antimony and bismuth and lead and a resin soluble in said stearates, said resin and said stearates being in solid solution in each other.

3. A coating composition comprising approximately: 65% of a mixture consisting of 40 parts of magnesium stearate and 60 parts of lead stearate; 30% of a resin soluble therein; and 5% of a wax plasticizer, all of said substances being in a solid solution in each other.

10 4. A coating composition comprising approximately: 65% of a mixture consisting of 50 parts of magnesium stearate and 50 parts of zinc stearate, said mixture being of the type composition obtained from the neutralization of stearic acid first with a magnesium alkali and then with a zinc alkali; 33% of a resin soluble in said mixture; and 2% of a liquid resin plasticizer.

16 5. A coating composition comprising approximately: 67.25% of a mixture consisting of 40 parts of magnesium stearate and 60 parts of lead stearate; 25.75% of a mixture of chlorinated diphenyl resins soluble in said mixture; and 7% of paraffin, all of said substances being in a solid solution in each other.

6. A coating composition comprising approximately: 55% of an acid stearate of a metal of the group consisting of zinc and cadmium and tin and magnesium and aluminum and antimony and bismuth and lead, 25% of a resin soluble therein, 15% of ethyl cellulose and 5% of a plasticizer. 5

7. A sheet material containing organic fibers, said fibers having therein a normal amount of moisture, said sheet material having a translucent, glossy, moisture proof coating adhering firmly to said sheet material without appreciable penetration thereof and comprising an eutectic mixture of at least two water-insoluble metallic soaps and a resin soluble in said soaps, said resin and said soaps being in solid solution in each other. 10 15

8. A normally solid printing ink, adapted for application in a molten condition, comprising: an eutectic mixture of at least two water-insoluble metallic soaps, a resin soluble in said soaps, an oil soluble dye, said soaps, resin, and dye being in solid solution in each other. 20

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