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COATING MATERIALS AND PROCESS FOR
MAKING THEM

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This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described, if patented, may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment to me of any royalty thereon.

This invention relates to coating materials and more particularly with such coating materials which may be used as a substitute for tin on metal containers to protect the metal from corrosion and to preserve products which may be placed in the containers.

At the present time the prospective shortage of tin has increased the demand for a substitute for this material for the purpose of coating metal containers. Although some substitutes are available at the present time, they possess objectionable features, such as the necessity for the surface of the metal to be first coated with a primer. The primer is necessary to obtain a better bond with the surface of the metal, or to prevent the outer coating from reacting chemically with the metal, or both. In some cases the coatings are unstable and tend to contaminate food products on long storage. Also, many coatings will not withstand high temperatures which are often necessary in packaging foods in metal containers. Many of the prior art coatings require the use of chemicals which are not available in times of war in the great quantities demanded by the canning industry.

The general object of this invention is the provision of a protective coating of the type mentioned and a process of making it which will obviate the difficulties mentioned above. The protective coating of this invention can be applied directly to the surface of metal containers, and it is insoluble, non-toxic, adherent, tough, flexible, and resistant to water, steam, alcohol, acids, and weak alkalies. This invention does not involve the use of materials which are or which may become scarce, insofar as it can be foreseen at present, in either normal times or in times of war.

The coating of this invention may be applied to metals, such as iron, steel, aluminum, tin, and various alloys, without the necessity of using a primer, and it has been found not to contaminate food in any way. Foods especially susceptible to taste contamination were found not to be affected at all. In using iron, the coating will adhere better if the surface of the iron is first subjected to a hot dip phosphate treatment.

In general, my invention comprises heating

a mixture comprising polylactylic acids (also known as polylactyllactic acids) and a drying oil, preferably in the presence of a catalyst, whereupon the mixture becomes resinified to a soft, elastic, and soluble material. It is to be understood that the term "drying oils" as used herein includes the class of oils known as "semi-drying oils," and oils which may become drying oils during the process of this invention. In general, any oil of this class may be used, such as castor oil, dehydrated castor oil, corn oil, linseed oil, tung oil, oiticica oil, Perilla oil, and soya bean oil. Examples of the catalysts which may be employed are, activated bauxite, cobalt salts (such as cobalt chloride), ferric oxide, chromic oxide, ferrous lactate, powdered iron, aluminum powder, magnesium turnings, magnesium methoxide, vanadium pentoxide, and cobalt oxide. The catalyst appears to catalyze both a condensation and polymerization reaction. A better product is formed if the mixture also includes a material such as fumaric acid or maleic anhydride. As the second phase of the process, the resinified material is then dissolved in a solvent, such as xylene, acetone, butyl alcohol, benzene, and glycol monomethyl ether, or a mixture of two or more of these solvents, to which is added a drying agent, which should be of a non-toxic nature so as to eliminate the possibility of any food poisoning. Suitable drying agents are zinc naphthenate, cobalt naphthenate, and manganese naphthenate. If desired, thinning agents may be used, such as toluene and petroleum solvents. This solution is then applied directly to the surface of the metal to be coated, such as by dipping, roller coating, and spraying, and then baked until hard. The time and temperature of baking will vary with the composition of the coating solution and the surface to which it is applied. Ordinarily the baking may be accomplished at a temperature between 150° C. and 260° C. in about 15 to 90 minutes.

The following examples will illustrate this invention, but it is to be understood that these examples do not in any way limit the scope of the invention. In these examples, all parts given are by weight.

Example 1

13.7 parts of polylactylic acids, 6.7 parts of castor oil, 2 parts of fumaric acid, and 2 parts of activated bauxite granules (20/60) mesh were mixed in an open vessel, while heating with continuous stirring, and the temperature raised to about 265° C. and maintained for about 7½ hours

until the resulting resin became viscous, soft, and elastic. A 50% yield of a brown rubbery resin was obtained. This resin was dissolved in a mixture of xylene and butyl alcohol to form a solution containing 30% of resin and then filtered. On the basis of the resin content, 0.2% of zinc naphthenate and 0.4% of cobalt naphthenate were added to form the final coating solution. The surface of an iron container was then coated with this solution by dipping. Excesses of the solution were permitted to drain off the metal surface and the remaining amount permitted to dry. The coated container was then baked for 90 minutes in an oven, the temperature of which was gradually increased from 150° to 210° C. The resulting coating was found to be tough and hard, to adhere excellently to the metal, and to resist decomposition by steam, acids, such as hydrochloric and acetic acids of various concentrations, alcohols, and weak alkalies, such as 1% sodium hydroxide.

The same coating solution was applied to a steel container and baked in the same manner, after which two additional coats were baked on in the same way over the first coat. Five gallon milk cans coated in this way were put into regular dairy service for a period of one to two months and were found not to contaminate the milk in any way.

Example 2

100 parts of polylactylic acids, 50 parts of soya bean oil, 5 parts of fumaric acid, and 1 part of activated bauxite granules were dissolved in an excess of xylene-butanol solvent mixture to aid in blending the ingredients and heated under a reflux condenser until the ingredients became blended. The condenser was then removed and the solvent was permitted to boil off. The temperature was increased to about 260° to 270° C. and maintained thereat for about 6 hours. The brown rubbery resin resulting was dissolved in a mixture of 50 parts of xylene and 50 parts of butanol to make a solid content of 30%, filtered, and 0.3% of zinc naphthenate and 0.6% of cobalt naphthenate were added to the solution. The same procedure as explained in Example 2 was followed in baking the resin on an iron surface, and the baked product was tested and found to be resistant against steam, weak alkalies, and alcohols.

Example 3

Same as Example 2, except that linseed oil was used instead of soya bean oil.

Example 4

100 parts of polylactylic acids, 50 parts of castor oil, 5 parts of maleic anhydride, and 1 part of ferric oxide were dissolved in a mixture of xylene and isoamyl alcohol. By gradually heating the mixture to 260° C. the solvent was boiled off. The mixture was then held at a temperature between 260° and 265° C. and stirred for about 3 hours until the resin became viscous. The resulting resinous composition was dissolved in benzene to make a coating solution. The solution was spread on an iron surface and baked 90 minutes in an oven, the temperature of which was gradually increased from 150° to 210° C.

Example 5

500 parts of polylactylic acids, 500 parts of castor oil, and 2 parts of concentrated sulphuric acid were mixed together and the temperature gradually raised to 260° C. over a period of 2½ hours

to blend the materials. The temperature was then held between 260° and 280° C. for about 3 hours, with constant stirring. The resulting resinous compound was then dissolved in benzene to make a coating composition containing 30% of the resin by weight. This material was spread on an iron surface and baked for 90 minutes in an oven, the temperature of which was gradually increased from 160° to 215° C. The baked coating showed characteristics similar to those described in the examples given above.

Example 6

The same as Example 1, except that ferrous lactate was used instead of activated bauxite granules.

Example 7

The same as Example 1, except that cobalt chloride was used instead of activated bauxite granules.

Example 8

The same as Example 1, except that magnesium methoxide was used instead of activated bauxite granules.

Having thus described my invention, I claim:

1. The process comprising heating a mixture comprising polylactylic acids and a fatty drying oil at a temperature and for a period of time sufficient to cause the mixture to become resinified to a soft and elastic material, followed by baking the material on a metal surface.

2. The process comprising heating a mixture comprising polylactylic acids and a fatty drying oil in the presence of a catalyst at a temperature and for a period of time sufficient to cause the mixture to become resinified to a soft and elastic material, followed by baking the material on a metal surface.

3. The process comprising heating a mixture comprising polylactylic acids, a fatty drying oil, and fumaric acid at a temperature and for a period of time sufficient to cause the mixture to become resinified to a soft and elastic material, followed by baking the material on a metal surface.

4. The process comprising heating a mixture comprising polylactylic acids, a fatty drying oil, and maleic anhydride at a temperature and for a period of time sufficient to cause the mixture to become resinified to a soft and elastic material, followed by baking the material on a metal surface.

5. The process comprising heating a mixture comprising polylactylic acids and an oil chosen from the group consisting of castor oil, dehydrated castor oil, corn oil, linseed oil, tung oil, oiticica oil, perilla oil, and soya bean oil at a temperature and for a period of time sufficient to cause the mixture to become resinified to a soft and elastic material, followed by baking the material on a metal surface.

6. The process comprising heating a mixture comprising polylactylic acids, castor oil, and fumaric acid in the presence of activated bauxite at a temperature and for a period of time sufficient to cause the mixture to become resinified to a soft and elastic material, followed by baking the material on a metal surface.

7. The process comprising heating a mixture comprising polylactylic acids and a fatty drying oil in the presence of activated bauxite at a temperature and for a period of time sufficient to cause the mixture to become resinified to a soft

and elastic material, followed by baking the material on a metal surface.

8. The process comprising heating a mixture comprising polylactic acids and a fatty drying oil in the presence of vanadium pentoxide at a temperature and for a period of time sufficient to cause the mixture to become resinified to a soft and elastic material, followed by baking the material on a metal surface.

9. The process comprising heating a mixture comprising polylactic acids and a fatty drying oil in the presence of salts of cobalt at a temperature and for a period of time sufficient to cause the mixture to become resinified to a soft and

elastic material, followed by baking the material on a metal surface.

10. A soft and elastic resin which can be baked on metal surfaces comprising the product formed by the reaction between polylactic acids and a fatty drying oil in the presence of fumaric acid.

11. A soft and elastic resin which can be baked on metal surfaces comprising the product resulting from the reaction between polylactic acids and a fatty drying oil in the presence of maleic anhydride.

12. A resin of the reaction product of polylactic acids and a fatty drying oil baked on a metallic surface.

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