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COATED METAL SURFACES AND PROCESS OF MAKING SAME

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This invention relates to coating compositions and metal surfaces coated therewith, and more particularly to improvements in coated containers for beer, ale and similar aqueous beverages.

Commercial canning of fruits and vegetables had its advent early in the 19th century and by the middle of the century canning was a large commercial enterprise. Today millions of tons of iron and steel are consumed annually in the fabrication of over 30 billion metal cans used for packaging a wide variety of products in modern canning plants where the cans are automatically filled and sealed at speeds as high as 300 per minute.

These metal containers became identified by the common name "tin can" because they had a thin surface coating of tin on the sheet iron or steel. The tin may range from about ½% of the total metal weight applied electrolytically to about 2% applied by the hot-dip process. The scarcity of tin and the necessity of its conservation stimulated the development of substitute coatings for the interior protection of sheet iron and steel containers.

Many organic coating compositions have been designed for application to the interior surface of metal cans to prevent corrosion. These interior coatings, for example, are based on vinyl, alkyd, urea-formaldehyde, melamine-formaldehyde and phenolic resins, cellulose nitrate lacquer, oleoresinous and ethylene polymer compositions, the type of coating being selected to conform with the corrosion resistance requirements of the packaged product and to meet the processing conditions. Although the primary purpose of the protective lining of the metal container is to prevent corrosion and contamination of the packaged material with corrosion products, one particular disadvantage of such contamination is alteration of the flavor of the material.

Retention of flavor and, in general, the retention of original quality in the initial palatable condition is the intent of the canning operation. Connoisseurs of food, beverages and liquors readily detect alterations in the taste and aroma of products, hence flavor retention has been an important consideration in the development of compositions for lining containers.

During the last decarde, packaging of beer and ale in metal containers has made a significant advance, through the development of coating compositions for protectively lining containers for packaging them. For example, plastic petroleum waxes, such as described in United States Patent No. 2,221,341, plasticized cellulose nitrate compositions disclosed in United States Patent No. 2,223,026, and vinyl chloride/vinyl acetate copolymer compositions disclosed in British Patent No. 506,808, have been used for coating the interior surfaces of beer cans.

Although such special coatings have provided an improved container for beer and the use of metal containers for packaging beer has been thereby extended, metal packages have not been universally accepted. Each critical consumer's personal taste determines his preference for canned, bottled or kegged beer. Even with kegged beer, the wooden barrel is being supplanted with aluminum or other metal kegs. The search continued for further improved coating compositions for beer cans which in use would render it exceedingly difficult for even the connoisseur or critical consumer to determine the type of coating used on the container.

It is an object of this invention to provide an improved coating composition for sheet metal and for interiorly lining metal containers. It is another object to provide sheet metal having an improved coating thereon. It is a further object to provide an improved lined container for packaging beer, ale and similar malt beverages of relatively low alcohol content. It is also an object to provide a process of manufacturing sheet metal and metal containers with an improved coating composition thereon. It is a more specific object to provide a ferrous container lined with an organic coating composition which is characterized by low transmission of iron to the packaged liquid contents.

These objects are accomplished by the incorporation of a particular polymer of ethylene within a critical concentration range of 0.1% to 0.5%, based on the coating solids, in a vinyl chloride/vinyl acetate copolymer composition, and by the application of said coating to the sheet metal parts which are to be fabricated as a container having an interior coating of the said composition.

The following are representative coating compositions suitable for carrying out this invention, the parts given being by weight.

EXAMPLE I

Vinyl chloride/vinyl acetate copolymer	20.00
Solvent mixture A	80.00
Polymer of ethylene dispersion A	.44
	100.44

The copolymer contained 85% vinyl chloride and 15% vinyl acetate by weight.

Solvent mixture A, for roller coat application of the composition, consisted of the following:

Toluol	45
Xylol	10
Methyl isobutyl ketone	40
Isophorone	5
	100

Other slow evaporating ketone solvents for the vinyl copolymer, such as methyl amyl ketone and cyclohexanone, may be substituted for the isophorone. The ethylene polymer was a low molecular weight type having an average molecular weight of about 8,000 to 10,000, and was a solid at room temperature.

The polymer of ethylene dispersion A was prepared by pebble mill grinding 23 parts of the polymer in 77 parts of xylol for 120 hours. Obviously, other concentrations of ethylene polymer and other solvents useful in the final coating composition may be used in the preparation of the dispersion.

The content of polymer of ethylene in the composition of Example I is equivalent to 0.5% based on the vinyl resin content.

The coating composition was applied by roller coating over sheet metal stock, which was previously roller coated with a base coat of orthodox varnish at a coating weight of 3 to 4 milligrams of solids per square inch and baked for about 10 minutes at an oven temperature of about 420° F. A typical varnish for use as a base coat for the interior coating of metal containers consists essentially of a maleic anhydride/polyhydric alcohol ester resin, china-wood oil and bodied linseed oil, with iron linoleate and manganese naphthenate present as driers. The vinyl

resin top coat composition modified with ethylene polymer was applied at a coating weight of 5 to 7 milligrams per square inch and baked at about 340° F. for 10 minutes. Container end parts were die stamped from this stock having both a base coat and a top coat baked thereon. Although the vinyl resin coating may be applied directly to the tin plate, sheet iron or steel, it is preferred to use a priming base coat to overcome adhesion deficiencies of the vinyl resin composition.

Container blanks cut from stock coated with primer are fabricated into cylindrical shells having a soldered or welded side seam to form the body of the container. The vinyl resin coating was applied to the interior wall of the cylinder by spray and baked at as high a temperature as could be tolerated without softening the solder at the seam and adversely affecting the lithographing inks on the exterior surface. The bake was for 10 minutes at about 290° F. Longer baking cycles may be used but it is preferred that the temperature should not be less than 280° F. to avoid adhesion difficulties. The baking temperature should preferably not exceed 300° F. when soldered seams and lithographed surfaces are involved. Temperatures as high as 350° F. may otherwise be used. Higher temperatures lead to degradation and decomposition of the vinyl resin, particularly when applied directly to the metal surface.

Although the aforementioned vinyl resin roller coat composition may be thinned with suitable solvent mixtures, such as about equal parts of toluene and methyl isobutyl ketone, for spray application, it is preferred to use a composition specifically designed therefor. The sprayable product should be formulated with solvents which are completely volatilized from the applied coating by the time the baking cycle is completed. A typical solvent mixture for the sprayable composition consists of the following:

Solvent mixture B:	
Toluol	37.5
Xylol	12.5
Methyl isobutyl ketone	50.0
	100.0

The copolymer of vinyl chloride and vinyl acetate is sprayable at a concentration of 15%. The aforementioned dispersion of ethylene polymer, added in the ratio of 0.33 parts per 100 parts of vinyl resin solution, is equivalent to 0.5% of ethylene polymer based on the vinyl resin at the said sprayable concentration.

The bottom end closure of the container is preferably double-seamed to the tubular wall, using a seam sealing compound to insure a hermetic seal. It is customary to supply the containers to the packager in the form of open-top cylinders and top closures. After filling, the top closure is also preferably double-seamed to the tube or cylinder, with the seam caulking compound completing the hermetic seal.

Such a container was filled with beer, hermetically sealed by seaming the top closure to the filled container, and thereafter the packaged beer was subjected to pasteurization and other normal processing operations.

The iron pick-up of the beer stored in contact with the coating represented by Example I was 0.45 parts per million.

The beer packaged in contact with the ethylene polymer modified vinyl copolymer resin retained its original palatable flavor after storage for six months. The same beer packaged in a container coated with the unmodified vinyl resin composition was altered in flavor or taste, although it was considered palatable. Packaging and storage in contact with the two types of container linings reflected no significant differences in other qualities of the liquid product, such as color and clarity, but storage of the beer in contact with the vinyl resin lining modified with ethylene polymer exhibited significantly less iron pick-up than the product packaged in contact with the unmodified vinyl resin coating.

Flavor changes during storage are believed to be due to several factors, among which are contamination with very small amounts of metal transferred from the container wall through the lining to the beer, leaching of flavor adulterants from the container lining by the beer, and adsorption of flavor-contributing components of the beer by the container lining.

EXAMPLE II

Vinyl chloride/vinyl acetate copolymer	20.00
Solvent mixture A	80.00
Polymer of ethylene dispersion A	.22
	100.22

The respective components of this composition were identical with those used in Example I. The content of polymer of ethylene in the composition is equivalent to 0.25 parts per 100 parts of vinyl resin at the sprayable concentration. Evaluation of the container coating having this concentration of polymer of ethylene yielded results which showed that the iron pick-up of beer stored in contact with the said coating for a period of six months was only 0.28 parts per million.

EXAMPLE III

Vinyl chloride/vinyl acetate copolymer	14.0
Vinyl chloride/vinyl acetate/maleic conjoint polymer	6.0
Solvent mixture C	74.8
Polymer of ethylene dispersion B	5.2
	100.0

The vinyl chloride/vinyl acetate copolymer was the same as that used in Examples I and II.

The maleic modified vinyl chloride/vinyl acetate conjoint polymer was of the type disclosed in United States Patent 2,329,456.

The polymer of ethylene dispersion B was prepared as follows:

Gel preparation: 30 parts of ethylene polymer were added to 70 parts of xyol heated to a temperature of about 210° F. and, the mixure was then raised to a temperature of about 250° F. to effect solution of the ethylene polymer. The solution solidified to a milky colored gel on cooling.

Dispersion preparation: 100 parts of vinyl resin solution of the following composition were charged into a pebble mill and 3.5 parts of the above described gel were added thereto. This composition was ground for about 120 hours.

Vinyl resin solution:	
Vinyl chloride/vinyl acetate copolymer	14.7
Vinyl chloride/vinyl acetate/maleic conjoint polymer	6.3
Solvent mixture C	79.0
	100.0

This composition may be charged into the pebble mill in the form of either the preformed solution or as the individual components. The dispersion contains 5% of ethylene polymer based on the vinyl resin content and the finished sprayable product of Example III contains .25% of ethylene polymer based on the vinyl resin content.

The ethylene polymer was the same as that used in Dispersion A.

The solvent mixture was of the following composition:

Solvent mixture C:

Toluol	45
Xylol	10
Methyl isobutyl ketone	40
Cyclohexanone	5
	100

The ratio of the two vinyl resins in the above example is in the proportion of 70 parts of the vinyl chloride/vinyl acetate copolymer and 30 parts of the maleic acid modified conjoint polymer. The proportion of maleic modified conjoint polymer may vary widely, but it is preferred that the content does not exceed that of the vinyl chloride/vinyl acetate copolymer where the coating is to come in contact with alcoholic beverages. The presence of the conjoint polymer of vinyl chloride, vinyl acetate and maleic acid with the vinyl chloride/vinyl acetate copolymer improves the adhesion characteristics of the coating composition. As with Examples I and II, the iron pick-up was significantly low.

Beer packaged and stored for six months in contact with a commercial unmodified vinyl resin lining increased 1.45 p. p. m. (parts per million) in iron content, but the improved container lining of this invention reduced the iron pick-up to 0.45 p. p. m. or less as shown in the following tabulation:

Percent Ethylene Polymer Based on Vinyl Polymer At Sprayable Concentration	Iron Pick-up in p. p. m.
0	1.45
0.13	0.41
0.25	0.28
0.50	0.45

These results show that the iron pick-up was reduced by at least 70% by incorporating a fractional percent of ethylene polymer, as a dispersion in an organic liquid. The preferred sprayable concentration of ethylene polymer is from 0.1% to 0.5% based on the vinyl resin content. Higher concentrations impart an undesirable frosty, non-uniform appearance to the baked film without yielding an advantageous reduction in iron pick-up.

The preferred composition contains ethylene polymer characterized by an average molecular weight in the range of 8,000 to 10,000. However, an average molecular weight as high as 13,000 or as low as 6,000 may be acceptably used. Such polymers are described in United States Patents 2,153,553 and 2,388,160.

Vinyl copolymer resins useful in this invention may vary from 80–90% vinyl chloride and 20–10% vinyl acetate, the average molecular weight being preferably in the range of 10,000 to 20,000. The conjoint polymer of vinyl chloride, vinyl acetate and maleic acid used in combination with the aforementioned copolymer may range in molecular weight from 6,000 to about 20,000 and have a content of 0.1–3.0% combined maleic acid and 80–90% combined vinyl chloride, the balance being vinyl acetate.

In the fabrication of the container, the orthodox varnish base coat may be substituted by any other resinous organic base coat which adheres to the metal substrate. The nature of the base coat is not pertinent to this invention, the object of its use being to provide a lining for metal containers which is more adherent than the vinyl resin composition when applied directly to the metal. The base coat may be omitted in instances where the adhesion of the vinyl resin coating direct to metal is considered adequate.

In addition to the aforementioned orthodox varnish base coat, primers based on polyether resins derived from the condensation of bis-phenol and epichlorohydrin have been found to be particularly useful as base coats in combination with the ethylene polymer modified vinyl resin top coat of this invention in the fabrication of containers for beer.

The use of the coating compositions of this invention as finishes for interior lining of metal containers for packaging of beer, ale and similar beverages has significantly improved the retention of the original quality of the packaged product during storage. The use of metal containers interiorly lined with the compositions of this invention may be extended to other liquid or watery products whose quality would be impaired if there were the normal transfer of metal from the metal substrate wall.

It is apparent that many different embodiments of the present invention can be made without departing from the spirit and scope thereof and it is not intended to be limited except as indicated in the appended claims.

We claim:

1. As a new article of manufacture, a ferrous metal sheet having a priming coat on at least one side, and superposed thereon a thin film of a composition comprising a resinous vinyl film-forming material of the group which consists of vinyl chloride/vinyl acetate copolymers, vinyl chloride/vinyl acetate/maleic acid conjoint polymers, and mixtures of a vinyl chloride/vinyl acetate copolymer and a vinyl chloride/vinyl acetate/maleic acid conjoint polymer, and from 0.1% to 0.5% of a solid polymer of ethylene based on the vinyl resin content of the said composition, the average molecular weight of the ethylene polymer being from 6,000 to 13,000.

2. As a new article of manufacture, a ferrous metal sheet having a priming coat on at least one side, and superposed thereon a thin film of a composition comprising a vinyl chloride/vinyl acetate/maleic acid conjoint polymer and from 0.1% to 0.5% of a solid polymer of ethylene based on the weight of the said conjoint polymer, the average molecular weight of the ethylene polymer being from 6,000 to 13,000.

3. As a new article of manufacture, a ferrous metal sheet having a priming coat on at least one side, and superposed thereon a thin film of a composition comprising a copolymer of vinyl chloride and vinyl acetate and from 0.1% to 0.5% of a solid polymer of ethylene based on the weight of the said copolymer, the average molecular weight of the ethylene polymer being from 6,000 to 13,000.

4. The article of claim 3 in which the average molecular weight of the ethylene polymer is 8,000 to 10,000.

5. The article of claim 3 in which the ratio of vinyl chloride to vinyl acetate is from 80–90% to 20–10%.

6. The article of claim 3 in which the ratio of vinyl chloride to vinyl acetate is 85% to 15%, and the average molecular weight of the ethylene polymer is 8,000 to 10,000.

7. The article of claim 3 in which the vinyl copolymer-ethylene polymer composition film is present in the amount of 5 to 7 milligrams per square inch.

8. The process of manufacturing a ferrous metal sheet material for use in beverage containers, wrappers and the like, which comprises applying to at least one side of the sheet material a liquid composition comprising a resinous vinyl film-forming material of the group which consists of vinyl chloride/vinyl acetate copolymers, vinyl chloride/vinyl acetate/maleic acid conjoint polymers, and mixtures of a vinyl chloride/vinyl acetate copolymer and a vinyl chloride/vinyl acetate/maleic acid conjoint polymer, from 0.1–0.5% of a solid polymer of ethylene based on the weight of the vinyl resin, and a volatile solvent mixture for the vinyl copolymer and the polymer of ethylene, and thereafter baking the said film at about 280°–350° F.

9. The process of manufacturing a ferrous metal sheet material for use in beverage containers, wrappers and the like, which comprises applying to at least one side of the sheet material a liquid composition comprising a vinyl chloride/vinyl acetate/maleic acid conjoint polymer, from

0.1–0.5% of a solid polymer of ethylene based on the weight of the vinyl resin, and a volatile solvent mixture for the vinyl copolymer and the polymer of ethylene, and thereafter baking the said film at about 280°–350° F.

10. The process of manufacturing a ferrous metal sheet material for use in beverage containers, wrappers and the like, which comprises applying to at least one side of the sheet material a liquid composition comprising a vinyl chloride/vinyl acetate copolymer, from 0.1–0.5% of a solid polymer of ethylene based on the weight of the vinyl resin, and a volatile solvent mixture for the vinyl copolymer and the polymer of ethylene, and thereafter baking the said film at about 280°–350° F.

11. The process of manufacturing sheet metal for use in beverage containers and the like, which comprises applying a varnish priming coat to a ferrous metal base, superimposing thereon a coating of a composition comprising a resinous vinyl film-forming material of the group which consists of vinyl chloride/vinyl acetate copolymers, vinyl chloride/vinyl acetate/maleic acid conjoint polymers, and mixtures of a vinyl chloride/vinyl acetate copolymer and a vinyl chloride/vinyl acetate/maleic acid conjoint polymer, from 0.1% to 0.5% of a solid polymer of ethylene based on the vinyl resin content of the said composition, the average molecular weight of the ethylene polymer being from 6,000 to 13,000, and a volatile solvent mixture for the vinyl copolymer and the polymer of ethylene, and baking the said film at about 280°–350° F.

12. A beverage container comprising a tubular portion provided with an end member hermetically sealed to the said tubular portion, the inner surfaces of the said container having a coating which comprises a resinous vinyl film-forming material of the group which consists of vinyl chloride/vinyl acetate copolymers, vinyl chloride/vinyl acetate/maleic acid conjoint polymers, and mixtures of a vinyl chloride/vinyl acetate copolymer and a vinyl chloride/vinyl acetate/maleic acid conjoint polymer, and from 0.1% to 0.5% of a solid polymer of ethylene based on the vinyl resin content of the said composition, the average molecular weight of the ethylene polymer being from 6,000 to 13,000.

13. A beverage container comprising a tubular portion provided with an end member hermetically sealed to the said tubular portion, the inner surfaces of the said container having a coating which comprises a vinyl chloride/vinyl acetate copolymer and from 0.1% to 0.5% of a solid polymer of ethylene based on the vinyl resin content of the said composition, the average molecular weight of the ethylene polymer being from 6,000 to 13,000.

14. A beverage container comprising a tubular portion provided with an end member hermetically sealed to the said tubular portion, the inner surfaces of the said container having a coating which comprises a vinyl chloride/vinyl acetate/maleic acid conjoint polymer and from 0.1% to 0.5% of a solid polymer of ethylene based on the vinyl resin content of the said composition, the average molecular weight of the ethylene polymer being from 6,000 to 13,000.

15. A coated metal article adaptable as a container for potable aqueous liquids comprising a ferrous metal substrate coated with an organic primer coat and superimposed on said primer coat, a cured coating comprising a resinous vinyl film-forming material of the group which consists of vinyl chloride/vinyl acetate copolymers, vinyl chloride/vinyl acetate/maleic acid conjoint polymers, and mixtures of a vinyl chloride/vinyl acetate copolymer and a vinyl chloride/vinyl acetate/maleic acid conjoint polymer, and 0.1% to 0.5% of a solid polymer of ethylene based on the weight of said copolymer, the average molecular weight of the ethylene polymer being from 6,000 to 13,000, said coated article when adapted as an interiorly-coated, liquid-confining container providing a barrier coat for inhibiting iron contamination of said potable liquid when it is in direct contact with said cured coating.

16. A method of preparing a coated metal article adaptable as a container for potable aqueous liquids which comprises the steps of superimposing a liquid coating composition comprising a resinous vinyl film-forming material of the group which consists of vinyl chloride/vinyl acetate copolymers, vinyl chloride/vinyl acetate/maleic acid conjoint polymers, and mixtures of a vinyl chloride/vinyl acetate copolymer and a vinyl chloride/vinyl acetate/maleic acid conjoint polymer, a solid polymer of ethylene whose average molecular weight is from 6,000 to 13,000, in an amount corresponding to from 0.1% to 0.5% based on the weight of said copolymer, and a volatile solvent mixture comprising at least one solvent for the vinyl copolymer and at least one hydrocarbon which is a solvent for the ethylene polymer at an elevated temperature over an organic primer coat on a ferrous metal substrate, heating said coating to evaporate the volatile solvents therefrom and further heating the coating at a curing temperature in the range of 280° F. to 350° F., the cured coating serving as a barrier coat for inhibiting iron contamination of the potable aqueous liquid in direct contact therewith when said article is adapted as an interiorly-coated, liquid-confining container.

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