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COATING COMPOSITION COMPRISING AT LEAST TWO VINYL POLYMERS AND LECITHIN

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1 Claim. (Cl. 220—64)

This invention relates to coating compositions and metal surfaces coated therewith adapted for fabrication into interiorly lined containers. More particularly the invention relates to improvements in interiorly-coated metal containers for packaging of aqueous beverages.

While a primary purpose of interiorly lining metal containers with the protective coating is to inhibit corrosion of the metal, it is equally important that the products of corrosion and the metal do not contaminate the packaged beverage or aqueous comestible. Although contamination of the packaged product generally is not sufficient to cause physiological harm when the product is used for human consumption, a small degree of contamination, which may be expressed in the magnitude of parts per million may be sufficient to alter the flavor of the product or detectably alter its appearance and thereby cause it to be less palatable.

A desired objective of the canning of various foods and beverages is the retention of the product in its initial palatable condition. Flavor retention of the packaged food or beverage in contact with the container lining has been an important consideration in the development of the protective coatings for interior lining of containers. These coatings in addition to providing anti-corrosion protection must be substantially free of their own contaminants which might alter the palatability of the packaged product.

The packaging of food in containers of tin coated iron or steel commonly known as "tin cans" has been successful for a long period of time. The packaging of beer, ale and other malt beverages in "tin cans" has not been entirely satisfactory, since the beverages have not fully retained their original quality and flavor when packaged in contact with conventional organic lining compositions. The iron content of beer will increase during storage in a "tin can" interiorly lined with most organic coatings, although there is no visual evidence of corrosion of the metal surface beneath the organic coating. While the increase in iron content is registered in parts per million, the increase is sufficient to reflect an alteration in the flavor and quality of the beverage.

An important object of this invention is to provide an improved organic coating composition for ferrous sheet metal, particularly for interiorly lining ferrous metal containers. Another object is to provide a ferruginous metal sheet having an improved organic coating thereon adaptable for fabrication as a metal container. A further object is to provide an improved container interiorly lined with an organic coating for packaging beer, ale and similar malt beverages. A more specific object is to provide a ferruginous metal container interiorly lined with an organic coating composition which is characterized by low transmission of iron from the metal container

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surface to the liquid packaged in the container. Still another object is to provide a process of manufacturing sheet metal coated with an improved coating composition adapted for fabrication as an interiorly lined container.

5 A further object is to provide a process for manufacturing metal containers with an improved organic coating as the lining for the interior surface thereof.

These objects are accomplished by incorporating in a liquid coating composition comprising a vinyl chloride polymer dissolved in a volatile organic solvent therefor, about 0.1% to 0.75%, based on the weight of the vinyl polymer, of an organic iron-sequestering agent which chemically combines with iron.

10 The more specific objects are accomplished by applying at least one coat of the vinyl chloride polymer coating composition containing lecithin as the iron-sequestering agent to primed tin coated iron or steel sheets which are to be fabricated into food and beverage containers having an interior surface coating of the vinyl chloride polymer composition. The top coat finish is preferably applied to the ferrous sheet metal preprimed with a baked varnish type primer.

The following examples are given by the way of illustration and not limitation. The indicated parts are shown on a weight basis.

Example I

A sheet of steel coated with .25 pound of tin per about 218 square feet (base box) of steel was primed on one side with the following primer composition:

	Parts by weight
Epon 1007—epoxypolyether resin (resinous reaction product of epichlorohydrin and diphenylol propane)	29.4
35 Diacetone alcohol	33.3
Butyl monoether of ethylene glycol	20.0
60% solution of butylated urea/formaldehyde resin in butanol	7.3
40 Isopropyl alcohol	10.0
	100.0

The primer composition may be colored with a fractional percent of a suitable heat stable soluble dye.

45 Sufficient of the primer composition was applied to deposit .014 gram per four square inch area. The primer was cured by baking 10 minutes at 420° F.

The following top coat composition was applied to the primed surface by roller application:

	Parts by weight
50 "Vinylite" VAGH	3.0
"Vinylite" VMCH	16.0
Methyl isobutyl ketone	46.0
Methyl amyl ketone	4.1
55 Toluol	22.4
Xylol	18.5
Solution of soya lecithin in methyl isobutyl ketone (.0475 parts of soya lecithin per 8.0 parts of methyl isobutyl ketone)	8.0475
60	118.0475

The "Vinylite" VAGH was a copolymer containing hydroxyl substituents having a composition corresponding approximately to 90 parts vinyl chloride, 5 parts vinyl acetate and 5 parts vinyl alcohol.

65 "Vinylite" VMCH was a tripolymer, the approximate composition of which may vary within the following limits 80-90 parts vinyl chloride, 7.0-19.9 parts vinyl

acetate and 0.1-3.0 parts maleic anhydride. Vinyl polymers of this type are described in U. S. Patent 2,329,456, issued September 14, 1943.

The concentration of soya lecithin in the above composition corresponds to 0.25% based on the weight of the vinyl polymer content of the coating composition.

The above top coat composition was applied to the primed tin plate by means of a roller to deposit about .025 gram per four square inch area. After drying to remove the volatile solvent the top coat was baked for 10 minutes at 330° F. The flexibility and adhesion of the coating to the tin plate was satisfactory. Blanks were cut from the top coated sheet to form the ends of the container.

Blanks were cut from the primed metal sheet, without the above top coating composition, and fabricated into open cylinders having a soldered or welded side seam to form the body of the container. The above top coating composition at spraying consistency was sprayed onto the primed interior wall of the cylinder. The sprayed top coat finish was applied at a coating weight in the range of about .020 to .030 gram per four square inch area and thereafter baked at an oven temperature of about 290° F. for about 10 minutes. Other baking conditions may be used, but it is preferred that the baking temperature does not exceed about 300° F. when the exterior surface of the cylinder is coated with a decorative lithographing varnish and the side seam is soldered. When the seam is welded and when the exterior surface is not lithographed, temperatures as high as 350° F. may be used. Higher temperatures lead to degradation of the vinyl coating. Baking cycles longer than 10 minutes may be used, but in use of longer curing cycles it is preferred that the baking temperature be at least about 280° F. Use of lower baking temperatures adversely affects the adhesion of the vinyl coating.

After the coated end closure was attached to the cylinder wall it was double-seamed thereto using a conventional seam sealing compound to insure a hermetic seal. The containers are supplied to the packager in the form of interiorly coated bottom-sealed cylinders and coated end-closures for sealing the top after the container is filled. After filling, the end-closure is sealed to the top of the container using seam sealing compound to complete the hermetic seal.

In the packaging of beer and similar aqueous alcoholic beverages, the contents of the sealed container are subjected to pasteurization and other normal processing operations.

As a control test the above Example I was repeated, without the soya lecithin in the top coat composition.

The beer in the can lined with the composition of Example I retained its original quality and taste after 9 months' storage and was significantly more palatable than the beer packaged in the can with the control coating without the lecithin in the lining. The hardness of the coating and adhesion to the tin plate was not altered when the beer was subjected to pasteurization in the containers.

Example II

Example I was repeated using .50% of soya lecithin in place of .25% and no objectionable iron taste was imparted to the beer after 9 months' storage in a container lined with the composition of Example II.

In an accelerated test designed to show the relative effectiveness of the iron-sequestering effect of lecithin in beer container coatings, the coating compositions of Example I, II and the control without the lecithin were applied to a glass plate, and baked or cured in a conventional manner. Thereafter the coating was stripped from the glass plate and immersed in a solution containing 25 parts of ferrous sulfate per million parts of water. This solution was buffered to a pH of about 4.0 to simulate the acidity of beer. The iron content of the stripped

coating before and after 21 days of immersion in the salt solution was measured. The results were:

	Iron Content of Stripped Vinyl Coating in Parts of Iron Per Million Parts of Coating (By Weight)		
	Lecithin Content, percent	Before Immersion	After 21 Days' Immersion in Ferrous Sulfate Solution
Control.....	None	31.0	380
Example I.....	.25	39.5	528
Example II.....	.50	42.0	520

A concentration of lecithin in the range of about 0.1 to 0.75% based on the weight of the vinyl polymer provides adequate sequestering of iron from the container, when aqueous beverages, such as beer, are packaged in direct contact with the vinyl coating over a ferrous substrate. Concentrations of lecithin greater than .75% result in blush formation in the coating as a result of pasteurization of the beer in the containers. Blushing first occurs where the coating is exposed to the vapor phase of the beer. Concentrations of lecithin less than 0.1%, in the interior lining, do not provide adequate protection to the beer from iron contamination.

Although the examples show the use of lecithin as an iron-sequestering agent with a mixture of two vinyl copolymers as the best mode of carrying out the invention it is not to be so limited. The "Vinylite" VMCH or the "Vinylite" VAGH may be used alone as the vinyl polymer. Vinyl polymers useful in the practice of this invention are the soluble polymers which can be dissolved in ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone and isophorone at a useful coating concentration. The copolymers of vinyl chloride and other ethylenically unsaturated monomers are preferred since they are sufficiently soluble in ketones to form useful coating compositions. The polymerization products of monomer mixtures preferably containing about 80% to 90% vinyl chloride, the balance of the mixture comprising a vinyl ester of a lower fatty acid, such as the formate, acetate, propionate or butyrate. Preferred vinyl polymers contain a small percentage of carboxyl substituents or acid anhydride substituents capable of supplying the carboxyl substituents. Such interpolymers are obtained by polymerizing monomer mixtures of vinyl chloride, vinyl ester and a copolymerizable aliphatic alpha, beta mono-olefinic carboxylic acid such as maleic acid, maleic half ester, maleic anhydride, acrylic acid, methacrylic acid, ethacrylic acid, phenylacrylic acid, itaconic acid or crotonic acid. The content of the polymerizable acid component preferably is no greater than about 5% by weight. Preferred vinyl polymers also include those having hydroxyl substituents. Polymers of this type generally are obtained by hydrolysis of the vinyl ester component of the interpolymers. The hydroxyl content is preferably no greater than about 10% by weight calculated equivalently as vinyl alcohol.

The vinyl polymers mentioned above are useful individually or mixtures thereof which are compatible in carrying out this invention. In vinyl polymer mixtures it is desirable that one of said polymers is an interpolymers having carboxylic or carboxylic-forming substituents.

Solvents suitable for formulation of the coating compositions include the conventional ketone solvents, such as methyl isobutyl ketone, methyl ethyl ketone, methyl amyl ketone, cyclohexanone, isophorone and these solvents in admixture with aromatic hydrocarbon such as toluol and xylol. The proportions of solvents and diluents are selected to meet application conditions, using fast evaporating solvent mixtures for spray application and slower evaporating mixtures for roller coat application.

The coating compositions for coating metal for fabrica-

tion into containers are generally applied at a non-volatile content in the range of about 15 to 20%, and sometimes as low as 10%.

Soya lecithin is the most readily available lecithin, but it will be understood that lecithin from other vegetable sources as well as eggs is also operative in the practice of this invention.

It will be understood that while the examples show the use of the vinyl polymers as the sole film-forming material of the compositions for lining containers, inert, innocuous vinyl plasticizers and other compatible film-forming materials may be present in minor proportion. Polyethylene is useful to impart abrasion resistance to the coating which is a desirable property during fabrication of the containers. The ends of the container are usually coated in flat sheets and are subjected to a certain amount of abrasion during fabrication of the container.

Although the coatings of this invention may be applied directly to the metal substrate to be used in the fabrication of the coated container, it is preferred to use the compositions of this invention as top coats over pre-primed metal substrate. While Example I shows the use of a particularly preferred primer composition, practice of the invention is not limited to substrate pre-primed with the described heat-convertible composition. Baking type orthodox varnishes, such as represented by a composition consisting 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, are suitable primers for use under the vinyl top coat composition. Primers are desirably used because they are characterized by stronger anchorage to the substrate than can be accomplished with the vinyl top coat composition.

Although the description for priming the sheet metal substrate and application of the vinyl polymer top coat show preferred coating weights applicable in the fabrication of lined containers, it will be obvious that for other purposes, the primer coat at conventional film thickness ranging from a fraction of a mil to 2 mils or even higher is useful. It is possible to apply the vinyl polymer composition of this invention to the primed or unprimed metal substrate in one or more coats to obtain a coating thickness which may range up to several mils. Spraying and rollercoating are methods of application used in the container industry, but any of the conventional coating methods used for the application of normally liquid coating compositions are useful.

The use of the coating compositions of this invention as top coat finishes for interior lining of metal containers

for packaging beer, ale and similar aqueous beverages has significantly improved the retention of the original quality of the packaged product during normal storage of the product in direct contact with the invention coating. The use of these improved, lined metal containers may be extended to other aqueous liquid products the quality of which would be altered if normal transfer of metal from the metal container wall to the packaged product were to occur.

It is apparent that many different embodiments of the 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 claim.

I claim:

- 15 A beverage container comprising a tubular ferrous metal wall portion provided with top and bottom ferrous metal end parts hermetically sealed thereto, the inner surfaces of said container having a baked composite finish thereon comprising a heat-converted primer coat on the metal surfaces, superposed on said primer a baked top
- 20 coat comprising a mixture of at least two vinyl polymers, one of said vinyl polymers being an interpolymer of vinyl chloride, vinyl acetate and a copolymerizable alpha, beta mono-olefinic dicarboxylic acid, said acid component of
- 25 the polymer being present in an amount up to about 5% based on the weight of the polymer, the second vinyl polymer being a copolymer of 80-90% by weight of vinyl chloride and vinyl acetate containing hydroxyl substituents corresponding in an amount no greater than
- 30 about 10% as vinyl alcohol based on the weight of the polymer, and lecithin in an amount ranging from about 0.1% to about 0.75% based on the weight of the said vinyl polymers in said top coat, said baked composite finish being resistant to blushing when exposed to aqueous
- 35 vapor heated to pasturization temperature.

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