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METHOD FOR APPLYING AND METAL COATING COMPOSITION OF A BUTADIENE RESIN AND ORGANIC DERIVATIVE OF TITANIUM

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Fig. 1

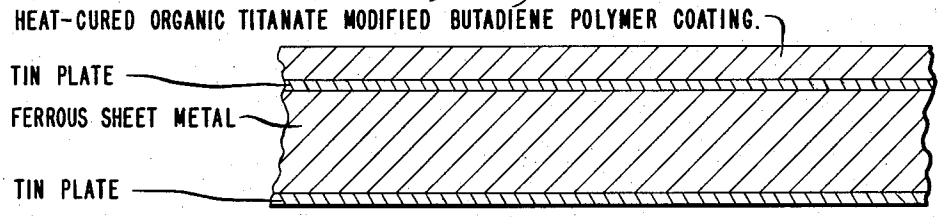
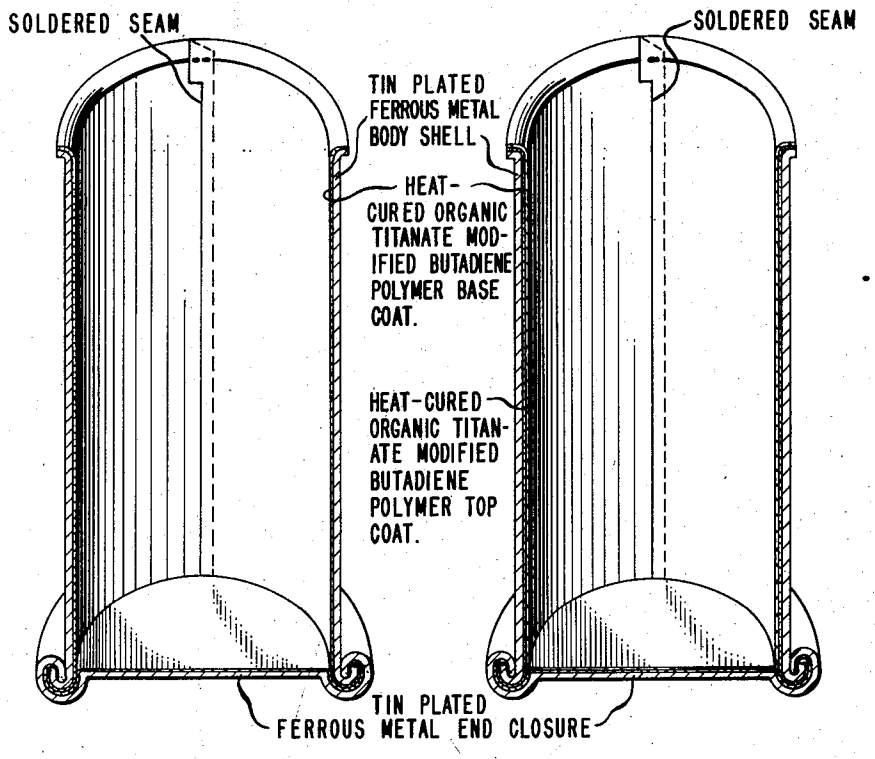


Fig. 2

Fig 3



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METHOD FOR APPLYING AND METAL COATING COMPOSITION OF A BUTADIENE RESIN AND ORGANIC DERIVATIVE OF TITANIUM

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17 Claims. (Cl. 220—64)

This invention relates to coating compositions and more particularly relates to coating compositions designed for use as a protective interior lining of metal containers used for packaging wet-pack food products and beverages which ordinarily are heat-processed or pasteurized in direct contact with the protective organic coating.

Although only a small fraction of the sheet metal used in the fabrication of the "tin can" is tin, for example, about 0.25 to about 1.5 pounds of tin per 218 square feet of surface area of an iron or steel metal sheet, the tremendous consumption of tin for container use has created a significant shortage of tin in view of the known limited world supply.

One method of conserving tin has been to minimize the thickness of the tin coating and supplement it where necessary with a superimposed protective organic coating, such as an oleo resinous varnish baked on the ferrous sheet metal substrate. Such organic-coated, tin-plated ferrous metal sheets are fabricated into interiorly coated metal containers which are particularly designed for packaging wet-pack food products which are heat-processed or pasteurized in the container in direct contact with the organic coating.

Organic coatings which are useful for this protective service must be innocuous, free from components which alter taste and odor, resistant to aqueous extracts of the wet-pack food products under the conditions associated with heat-processing or pasteurization and during lengthy storage of the packaged food in the container.

High speed operations of container fabrication from the precoated sheet metal imposes other important qualifications on candidate organic coatings. A particularly important qualification is that the cured organic coating must be adequately flexible to be fracture-resistant under the conventional mechanical operations associated with stamping or cutting container body and end-closure parts from the precoated sheet metal and fabricating the container parts into an interiorly coated container. The organic coating must also be adequately flexible to be fracture-resistant under the heat and pressure conditions to which the coated container is subjected during heat-processing of the food products.

Lack of fracture-resistance is a common failure in many potentially useful coatings and when these coatings are modified to improve the flexibility to provide adequate fracture-resistance, they ordinarily are deficient in the properties pertinent to food-processing.

Conventional oleoresinous varnishes currently used commercially as container coatings are acceptable in fracture resistance and moderately resistant physically and chemically under the conditions encountered in heat-processing of wet-pack foods in the container, but improvement in these properties is desirable to provide greater margin of protection in food preservation.

The primary object of this invention is to provide a butadiene polymer coating composition having the aforementioned qualifications desirable in a coating composition designed for use as an interior coating for metal

containers. A more specific object is the provision of a butadiene polymer coating composition, which applied at an effective protective thickness on sheet metal container parts, is adequately flexible to be resistant to fracturing under the mechanical operations involved in fabricating an interiorly coated container from the precoated parts. Another important object is the provision of a metal container, having on the interior surface thereof, a protective organic coating which is fracture-resistant under conditions of metal expansion and contraction caused by heat processing of wet-pack food and beverage products in the container. A further object is to provide the aforementioned type of container the interior coating of which is physically and chemically resistant to attack by the aqueous extracts of such food and beverage products processed and stored in direct contact with the protective organic coating. Still another object is to provide a method of protectively coating a metal sheet substrate used in the fabrication of interiorly coated metal containers designed for use in the packaging of wet-pack food and beverage products.

The objects of this invention are accomplished by applying to at least one surface of a ferrous metal sheet substrate a liquid coating composition comprising (A) a butadiene polymer selected from the class consisting of (1) homopolymers of butadiene-1,3, (2) copolymers of butadiene-1,3 and styrene and (3) said homopolymers and said copolymers modified with an anhydride of an unsaturated dicarboxylic acid selected from the class consisting of maleic anhydride and citraconic anhydride and (B) at least one substantially non-volatile, organic solvent-soluble organic derivative of titanium selected from the class consisting of (1) orthotitanate esters of aliphatic monohydric alcohols, (2) orthotitanate esters of 2,3-di-organo-substituted 1,3 diols, (3) orthotitanate esters of enolizable beta-ketoacid esters and (4) titanium acylates of fatty oil acids; and heating the coated substrate to cure the coating thereon

The accompanying drawings illustrate utility of the invention coating compositions as a can coating wherein:

Fig. 1 is a cross-sectional view of a flat sheet of tin-plated ferrous sheet metal of the type used in the fabrication of tin cans, the metal substrate having a heat-cured coating thereon comprising butadiene polymer and an organic titanate.

Fig. 2 is a cross-sectional view of a tin-can consisting of a cylindrical body shell and an end-closure sealed thereto; the body shell, being fabricated from the precoated sheet metal described in Fig. 1 and having the heat-cured coating as an interior lining or base coat.

Fig. 3 is a cross-sectional view of a tin-can corresponding to the article in Fig. 2 further having a heat-cured superimposed coating comprising a butadiene polymer and an organic titanate, the top coat being applied after the seam of the base-coated body shell was soldered and an end-closure was sealed to one end of the body shell.

The following specific examples are given by way of illustration and not limitation. The parts and percentages throughout the specification and claims are expressed on a weight basis unless stated otherwise.

Example 1

	Parts by wt.
Butadiene polymer	42.50
Mineral spirits (B. R. 145° C. to 215° C.)	56.63
Tetra(2-ethylhexyl) orthotitanate	.85
Silicone fluid—General Electric SF-03	.02
	100.00

The butadiene polymer was a homopolymer of butadiene-1,3 having an average molecular weight of about 1500. This homopolymer was prepared according to the

teachings of Miller U. S. Patent 2,708,639 in which process the butadiene-1,3 was polymerized in the presence of BF_3 etherate water catalyst.

The silicone fluid was identified as a low viscosity methyl siloxane polymer. Use of the silicone fluid is optional, but it functions advantageously as a wetting agent to facilitate wetting of the ferrous metal sheet with the butadiene polymer coating composition. Eye-holing or formation of islands in the dry coating results when the metal substrate is not properly wet with the liquid coating. Use of the silicone fluid remedies this condition.

In the preparation of the product of Example 1, the butadiene polymer was predissolved in the mineral spirits and thereafter the other components of the composition were added and mixed until the product was uniform.

This product was applied by flow-coating to one surface of a sheet of .25 electrolytically tin-plated steel, that is, the sheet steel had a tin plating thereon corresponding to .25 pound of tin to about 218 square feet of metal sheet surface, and partially dried by volatile loss of mineral spirits from the wet coating. Thereafter the coated ferrous metal sheet was heated in an oven for 10 minutes at 385° F. to cure the coating. The cured coating at a preferred dry coating weight of 5.5 milligrams per square inch of surface was pale golden color, clear, transparent, adherent to the metal substrate, and continuous, that is, free from eye-holing or islands.

The sheet metal stock coated with the cured product of Example 1 was stamped into container body parts and container end-closures for subsequent fabrication as a cylindrical metal container having the metal surface coated with the cured organic coating as the interior surface of the container.

Representative samples of the stamped container parts were examined for coating fracture which may be caused by the mechanical operations of stamping the coated metal sheet. Because fracturing is not easily detected by the unaided eye, fracturing was conveniently determined by a conventional chemical test used by the container industry in which the test part is immersed in a copper sulfate plating bath for 10 minutes during which time the copper sulfate electrolyte will penetrate through any fractures to stain and plate out copper on the metal substrate at the fractures in the coating.

A suitable electrolyte bath for this test consists of 750 grams of $CuSO_4 \cdot 5H_2O$ and 190 grams of commercial concentrated hydrochloric acid diluted to one gallon with distilled water.

In carrying out the test, exposed metal and surface areas other than the test area were protected with a paraffin coating applied as a hot-melt. After immersion in the electrolyte, the test parts were rinsed with water and examined for evidence of staining or copper plating. The tested container parts coated with the product of Example 1 were substantially free from copper staining, indicating excellent resistance to fracturing under the mechanical operations of container fabrication. Fracture-resistance was superior to that ordinarily accepted by the trade as representative of organic coatings in commercial use for can coating.

The coated container parts were fabricated as a container constituting a cylindrical body part with a soldered side seam and an end-closure double-seamed to the body part with the coated surfaces of the metal constituting the interior surface of the containers. The resulting interiorly coated containers were tested by actually heat-processing representative wet-pack food products in the container in direct contact with the organic coating according to established test methods used by the container industry. Sour cherries, pumpkin, corn and pork were used as representative food products in the processing tests. Depending on the particular processed food product, heat-processing was carried out in a steam pressure cooker under conditions ranging from about 15 minutes at 210° F. to 150 minutes at 250° F. with the pressure as high as that corresponding to steam at a temperature within the indicated range. Each of the hermetically sealed food-filled containers had about one quarter inch of head space as air.

All the test containers having a content of processed food products were immediately cooled to room temperature after heat-processing and stored for at least 18 hours before representative sealed containers were opened for initial examination. Other series of hermetically sealed test containers filled with processed food were stored for subsequent inspection after periods of 1, 2 and 3 months storage at room temperature and storage at 100° F., and after 1, 2 and 4 weeks storage at 120° F.

After the respective storage periods, the containers were opened and the interior surfaces thereof were examined for blistering, blushing, discoloration or staining, adhesion to the metal substrate, flaking and softness. In the initial examination after heat-processing of wet-pack food in the container, examination was also made for fracturing of the coating as may be caused by expansion and contraction of the metal container during processing of the food.

The cured coating of the product of Example 1 was resistant to physical and chemical attack by aqueous extracts or juices of wet-pack food products during heat-processing in the container and during the respective storage periods of such food extracts and parent food products in direct contact with the organic coating. The coating was blush-resistant and blister-resistant. For all practical consideration, the coating was unchanged from its initial quality in reference to hardness, flexibility, color, clarity and adhesion. Slight sulfur-staining was detected on the interior surface of containers in which pork was heat-processed and stored. The coating exhibited advantageous improvement in reference to fracture-resistance and physical and chemical resistance to aqueous food extracts and to the conditions associated with heat processing of the wet-pack food in comparison with a conventional oleoresinous varnish used to interiorly coat food containers in the same described manner. There was no evidence of deleterious effect of heat-processing and storage on the food packaged in the test containers.

The product of Example 1 offered an additional advantage in that it was adequately cured at a temperature at least 25° F. lower than that used to cure conventional oleoresinous varnishes designed for can coating, which varnishes ordinarily are cured by baking at a temperature of about 410° F.

Comparable results were obtained in reference to fracture-resistance during mechanical operations and physical and chemical resistance under food processing operations and during storage, when the product of Example 1 was applied to other sheet steel having a surface coating of tin thereon ranging from .25 to 1.5 pounds per 218 square feet of surface, applied either electrolytically or by hot-dip, and the resulting organic-coated metal substrates were fabricated as an interiorly coated container.

Example 2

	Parts by wt.
Butadiene homopolymer (same as used in Example 1)	35.00
Mineral spirits (B. R. 145° C. to 215° C.)	33.58
High solvency petroleum naphtha (B. R. 130° C. to 195° C.)	30.00
Tri(2-ethylhexyl) orthophosphate	.70
Tetra(2-ethylhexyl) orthotitanate	.70
Silicone fluid—General Electric SF-03	.02
	100.00

The composition of the product of this example is similar to that of Example 1, but it includes tri(2-ethylhexyl) orthophosphate, which in addition to its plasticizing effect functions to accelerate the cure of the product on heating, and additional hydrocarbon diluent of the xylol-substitute type high solvency petroleum naphtha to provide a sprayable product.

The several components of the composition were mixed until the product was uniform.

Metal containers were fabricated from container parts precoated with the product of Example 1 applied as described at a dry coating weight of about 3 milligrams per square inch of surface and cured by heating 10 minutes at 385° F. The resulting interiorly coated containers were further coated by spraying on their interior surfaces the product of Example 2 which was applied at a dry coating weight of about 5 milligrams per square inch of surface to provide a total dry coating weight of about 8 milligrams per square inch. The final coating was cured by heating the coated container for 10 minutes at about 300° F. Representative containers of this type were filled with beer, sealed and subjected to conventional pasteurization by heating for 30 minutes at 150° F. Examination of the interior surface of representative containers opened 24 hours after pasteurization and after 3 months of storage revealed that the protective coating was unaffected by pasteurization and storage in contact with the aqueous alcoholic malt beverage. The quality of the stored beer was not distinguishable from samples of the same beer bottled in glass.

The product of Example 2 was similarly applied by spraying to plain sheet steel, which did not have a surface coating of tin, at various coating weights ranging up to about 10 milligrams dry weight per square inch of coated surface and was cured under conditions ranging from 60 minutes at 250° F. to 5 minutes at 420° F. The resulting cured coatings were found to be fracture resistant and flexible. Curing under these respective conditions was found to provide substantially the same degree of cure as accomplished by heating the coated substrate at 385° F. for 5 to 15 minutes.

Organic coated plain sheet steel is not used in the fabrication of containers designed for wet-pack food packaging because the coating weight of protective organic coating ordinarily applied over tin-plated sheet steel is not adequately protective against aqueous food extracts in the absence of the tin-plating which is at a coating weight of at least about .25 pound of tin per 218 square feet of surface. Coating weights of the butadiene polymer coating composition greater than 8 milligrams dry weight per square inch can be satisfactorily applied to plain sheet steel to provide adequate protection against food-processing conditions, but application of a multiplicity of coats ordinarily is required to provide such higher coating weights. At the conventional coating weight of about 2 to 8 milligrams dry weight per square inch of surface applied to plain sheet steel, the organic coated sheet steel can be fabricated into satisfactory containers which have general utility except for packaging wet-pack food products.

Because processing of pork and corn ordinarily cause some staining of the interior surface of the container due to the sulfur content of these food products, it is desirable to include in the coating a sulfur-sequestering agent, such as zinc oxide, which sequesters the sulfur in an apparently non-staining or non-discoloring form. Sulfur sequestered as zinc sulfide is visually indetectable in the presence of zinc oxide. Example 3 below is representative of using zinc oxide as a sulfur sequestering agent in the invention compositions.

Example 3

	Parts by wt.
Butadiene homopolymer (same as used in Example 1)	35.70
Mineral spirits (B. R. 145° C. to 215° C.)	51.58
Tetra(2-ethylhexyl) orthotitanate	.80
Silicone fluid—General Electric SF–03	.02
Zinc oxide paste	11.90
	100.00

The zinc oxide paste had the following composition:

	Parts by wt.
Lead-free zinc oxide pigment	41.0
Butadiene homopolymer (same as used in Example 1)	23.0
Mineral spirits (B. R. 145° C. to 215° C.)	36.0
	100.0

The zinc oxide was dispersed in the hydrocarbon solution of butadiene polymer in accordance with a conventional method of dispersing pigment in paste form.

In the preparation of the product of Example 3, the components were mixed until the product was uniform. The zinc oxide content of the product was about 12.7% by weight based on the polymer content.

The product of this example was flow-coated on electrolytic tin-plated sheet steel in the same manner as described in Example 1. The coated metal sheet was fabricated into an interiorly coated container and the container and parts thereof were tested as described above. The resulting containers were found to be fully acceptable for packaging wet-pack food products which are heat-processed in the container. The results in the specific tests were equivalent to those obtained with the product of Example 1, with the added advantage that the interior coated surface of the container was resistant to sulfur-staining by pork and corn products.

Example 4

	Parts by wt.
Butadiene polymer—Butarez 25 oil	40.0
Mineral spirits (B. R. 145° C. to 215° C.)	57.0
Octyleneglycol titanate—Du Pont's OGT–41-solution. 69% by wt. in butanol	3.0
	100.0

The several components of the composition were mixed until the product was uniform.

The Butarez 25 oil, commercially available from Phillips Petroleum Company, was a homopolymer of butadiene-1,3, having an average molecular weight of about 1500. The octyleneglycol titanate OGT–41 was the commercially available tetra ester of orthotitanic acid and 2-ethylhexanediol-1,3 described in Du Pont Titanium Organics—Titanium Chelates.

The product of this example was flow-coated on electrolytic tin-plated sheet steel at a dry coating weight of about 5 milligrams per square inch and cured by heating the coated sheet metal for 10 minutes at 385° F. The organic-coated sheet metal was satisfactorily fabricated into interiorly lined containers which in turn were found to be entirely satisfactory as containers designed for use in packaging wet-pack food products. Fracturing tests and food processing tests yielded results which were comparable with those obtained with the product of Example 1.

Example 5

	Parts by wt.
Butadiene polymer—Butarez 25 oil	40.0
Mineral spirits (B. R. 145° C. to 215° C.)	57.3
Octyleneglycol titanate—Du Pont's OGT–21 solution. 76% by wt. in butanol	2.7
	100.0

This product was identical in composition with that of Example 4 except that the titanate OGT–21 was substituted on an equal weight basis for OGT–41. OGT–21 was the commercially available chelated titanium ester prepared by alcoholysis of tetrabutyl titanate in the proportion of one mol of the tetrabutyl titanate per two mols of 2-ethylhexanediol-1,3. Hence, this chelated titanium derivative contained a pair of butoxy substituents in addition to the two chelated substituents per titanium atom.

Evaluation of this product yielded results which were identical with those obtained with the product of Example 4.

Example 6

	Parts by wt.
Butadiene homopolymer—(same as used in Example 1)	37.50
Mineral spirits (B. R. 145° C. to 210° C.)	59.48
Tetra(2-ethylhexyl) Orthotitanate Solution—50% by wt. in 2-ethylhexanol	1.50
Ethylacetoacetate	1.50
Silicone fluid—General Electric SF–03	.02
	100.00

The components of the composition were mixed until the product was uniform.

In this composition a titanium chelate was formed in situ by ester interchange between the tetra(2-ethylhexyl) orthotitanate and the enolizable ethylacetoacetate, a beta-ketoacid ester.

Evaluation of the product of Example 6 as an interior coating for food-processing containers as described in Example 1 yielded excellent results which were equal to those obtained with the products of the preceding examples.

Example 7

	Parts by wt.
Butadiene polymer—Butarez 25 oil	40.0
Mineral spirits (B. R. 145° C. to 215° C.)	58.0
Polymeric isopropoxytitanium oleate	2.0
	100.0

The components of the composition were mixed until the product was uniform.

The polymeric isopropoxytitanium oleate was the commercially available TROLA isopropoxytitanium oleate described in Du Pont Titanium Organics—Titanium Acylates. This titanium acylate contains an average of about one acylate group per titanium atom, the remaining substituents on the titanium atoms being isopropoxy groups.

The product of this example was applied by flow-coating on electrolytic tin-plated sheet steel to the preferred dry coating weight of about 5 milligrams per square inch of coated surface and evaluated as an interior coating for containers used in wet-pack food packaging and heat-processing as described in Example 1. The product was found to be suitable for can coating and the individual tests showed that the containers coated therewith were significantly better than containers interiorly coated with conventional oleoresinous varnishes.

Example 8

	Parts by wt.
Butadiene polymer—Butarez 25 oil	40.00
Maleic anhydride	.25
Mineral spirits (B. R. 145° C. to 215° C.)	58.55
Tetra(2-ethylhexyl) orthotitanate	1.20
	100.00

In the preparation of this product, the oily butadiene polymer was run to a temperature of 210° F. in 30 minutes, the maleic anhydride was slowly added to the hot oil while the temperature was raised to 300° F. in 20 minutes and the mixture was vigorously agitated while

the temperature was held at 300° F. for 45 additional minutes. Thereafter, the mixture was cooled by dilution with the mineral spirits and the tetra(2-ethylhexyl) orthotitanate was added and uniformly mixed into the composition to complete the product.

This product was flow-coated and cured on electrolytic tin-plated sheet steel as described in Example 1 and, in turn, fabricated as an interiorly coated container. The container parts were examined for fracturing and the resulting container was evaluated as previously described for heat-processing of wet-pack food products. Containers interiorly coated with this product were found to be equivalent to those coated with the product of Example 1.

Citraconic anhydride substituted on an equal weight basis for the maleic anhydride in the preparation of the product of Example 8 provides a coating composition equally suitable for use in interiorly coating containers for food packaging.

Example 9

	Parts by wt.
Butadiene/styrene copolymer	43.5
High solvency petroleum naphtha (B. R. 130° C. to 195° C.)	28.2
Mineral spirits (B. R. 145° C. to 215° C.)	27.0
Tetra(2-ethylhexyl) orthotitanate	1.3
	100.0

The copolymer had a molecular weight of about 1200 and contained about 90.8% by weight of polymerized butadiene-1,3 and 9.2% polymerized styrene, the polymerization being carried out in the presence of sodium/naphthalene catalyst.

The product of this example applied to a tinplated ferrous sheet metal substrate and evaluated as previously described in Example 1 was found to be adequately fracture-resistant and flexible and suitably resistant chemically and physically for use as an interior coating of containers designed for packaging food products which ordinarily are heat-processed in the container.

Commercially available Standard Oil Company's "C" Oil, a copolymer of butadiene-1,3 and styrene comparable to that used in Example 9, substituted on an equal weight basis for the copolymer in that example provides a product which is equivalent in quality when evaluated as an interior can coating. This copolymer substituted on an equal weight basis for the Butarez 25 Oil, butadiene homopolymer, in Example 8 and treated with maleic anhydride as described therein provides an equivalent product suitable for container coating.

As indicated by the examples, a wide variety of butadiene polymers can be used in the practice of this invention. Useful polymers include homopolymers of butadiene-1,3 prepared by polymerization catalyzed by either sodium, boron trifluoride, boron trifluoride etherate complex or boron trifluoride etherate complex and water. These homopolymers can be prepared by either a single stage process or by a two-stage process in which the preformed polymer is subjected to further treatment with a Friedel-Crafts catalyst as described in Garber U. S. Patent 2,560,164 or subjected to heat-bodying. Copolymers of butadiene-1,3 and styrene in which the butadiene-1,3 component is at least 75% by weight of the copolymer can also be used. Preparation of useful copolymers of this type is described in Gleason U. S. Patent 2,672,425. These homopolymers and copolymers treated with either maleic anhydride or citraconic anhydride in an amount ranging up to about 2% based on the weight of the polymer can also be successfully used in the practice of this invention. Acid anhydride modified butadiene polymers of this type are described in Gleason U. S. Patent 2,652,342 and in Miller U. S. Patent 2,708,639. Modification with the acid anhydride can be carried out either as an after-treatment of the pre-

formed polymer or during the polymerization of the butadiene polymer. Polymers of butadiene in which the content of modifying maleic or citraconic anhydride is greater than 2%, such as up to 10%, can be used in admixture with unmodified butadiene polymer in an amount such that the total content of the acid anhydride does not exceed 2% based on the total weight of the butadiene polymer and preferably is no greater than about 1% on this basis.

The preferred butadiene polymers are oily liquid polymers having an average molecular weight ranging from about 1000 to about 5000. Satisfactory coatings can also be prepared from butadiene polymers having an average molecular weight ranging from about 700 to about 20,000. Higher molecular weight polymers are operative in the practice of the invention, but the non-volatile content of the resulting coating composition is too low at conventional application viscosity for practical use, particularly where it is desirable to apply an adequately protective coating weight in a single coat.

The liquid coating compositions of this invention can be satisfactorily applied by conventional means at a non-volatile content as high as 70% by weight. While the primary utility of these products in the container field requires a substantially high non-volatile content at application viscosity to provide a preferred dry coating weight of about 2 to 8 milligrams per square inch of surface in a single coat, the products can contain as little as 10% non-volatile content and be recognized as practical where application by a plurality of coats is acceptable.

A wide variety of substantially non-volatile, organic-solvent-soluble organic derivatives of titanium are useful in modifying the butadiene polymer in the practice of this invention. Ordinarily at least 1% of the organic titanium derivative based on the weight of the butadiene polymer is required to register a practical improvement in the properties of the coating derived from the butadiene polymer. No significant advantages were found in using more than 10% by weight of the organic titanium derivative based on the weight of the butadiene polymer although no adverse effects were observed when the concentration was as high as 15% by weight on the indicated basis. A concentration in the range of about 1.5% to 6.0% based on the weight of the butadiene polymer is preferred.

Tetra(2-ethylhexyl) orthotitanate is a particularly preferred member of the group of substantially non-volatile orthotitanate esters of aliphatic monohydric alcohols useful in the practice of this invention. Any of the orthotitanate esters of 6 to 20 carbon atom aliphatic monohydric alcohols can be used in place of the preferred 2-ethylhexyl orthotitanate. Volatility of the lower esters, such as the titanate esters of ethyl, isopropyl, butyl or amyl alcohol is too significant for satisfactory use as the sole organic titanium derivative in the invention compositions. However, these volatile esters can be present in minor proportions in admixture with the substantially non-volatile organic titanium derivatives.

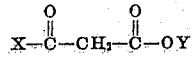
Orthotitanate esters of 2-ethylhexanediol-1,3 are particularly preferred among the titanium chelates useful in the practice of this invention. Other useful titanium chelates can be prepared following the teachings of Bostwick U. S. Patent 2,643,262 where these chelates are prepared by alcoholysis of a tetraorthotitanate ester of a lower alcohol with a 2,3 diorgano-1,3 diol having the general formula

$$R—CHOH—CHR'—CH_2OH$$

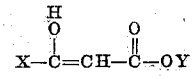
where R and R' are alkyl hydrocarbon radicals whereof the sum of the carbon atoms in R and R' total from 3 to 7 carbon atoms.

These chelated titanium derivatives can be formed in situ in the liquid coating composition by alcoholysis between the titanium derivative introduced into the liquid coating composition as a tetraorthotitanate ester of a volatile alcohol and a 2,3 diorgano-1,3 diol of the aforementioned general formula.

Another useful class of titanium chelates are the orthotitanate esters of enolizable beta-ketoacid esters of which the orthotitanate ester of ethylacetoacetate is preferred. These chelates can be formed conveniently in situ in the liquid coating composition by alcoholysis between ethylacetoacetate or a similar enolizable beta-ketoacid ester introduced into the composition in combination with a tetraorthotitanate ester of a volatile alcohol. Useful chelating beta-ketoacid esters are of the general formula:

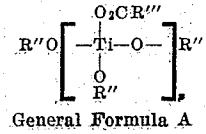


which is enolizable to:



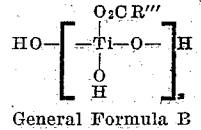
where X and Y are each saturated hydrocarbon radicals having from 1 to 6 carbon atoms, X and Y being alike or different. Typical beta-ketoacid esters useful in the alcoholysis reaction include for example the methyl, ethyl, propyl, butyl, amyl, hexyl, and cyclohexyl alcohol esters of acetoacetic acid (beta-oxo-butyric acid), beta-oxo-valeric acid, beta-oxo-caproic acid, beta-oxo-caprylic acid, and beta-oxo-cyclohexanepropionic acid.

Isopropoxy titanium oleate and similar liquid titanium acylates are preferred among the useful titanium acylates of fatty oil acids. The liquid titanium acylates offer the advantage of being easily mixed with the butadiene polymer solution as compared with the waxy solid titanium acylates. The titanium acylates can be either monomeric or polymeric materials prepared by reacting a monomeric or polymeric orthotitanate ester of a lower alcohol with an 8 to 20 carbon atom fatty acid as described in Langkammerer U. S. Patent 2,621,193, Haslam 2,621,195 and Boyd 2,666,772. Titanium acylates are also referred to as titanium ester anhydrides in which the orthotitanic acid is partially anhydrided with the fatty acid and partially esterified with a monohydric alcohol. The preferred titanium acylates useful in this invention are of this latter type and are characterized by the general formulas:



General Formula A

and



General Formula B

where R'' is a hydrocarbon radical of a lower aliphatic monohydric alcohol such as isopropyl alcohol or butyl alcohol, and the radical $R'''CO_2$ is the fatty acid acyl radical. x is a digit ordinarily in the range of 1 to 100, the average molecular weight of the polymeric titanium acylate ordinarily ranging up to about 40,000. Titanium derivatives of General Formula B are obtained from a product of General Formula A by hydrolysis. Titanium acylates of General Formula A can also be subjected to alcoholysis for replacement of the R'' group with a hydrocarbon radical having a larger number of carbon atoms to provide a still greater variety of useful titanium acylates. In addition to the isopropoxy titanium oleate, useful polymeric and monomeric titanium acylates include butoxy titanium oleate, isopropoxy- and butoxy-titanium acylates of lauric acid, coconut oil acids, soya oil acids, linseed oil acids, castor oil acids and tall oil acids.

Volatile inert organic mutual solvents for the butadiene polymer and the organic titanium derivative are preferably hydrocarbon solvents. Any of the volatile aromatic hydrocarbons, aliphatic hydrocarbons and mixtures thereof which ordinarily have a boiling range within the limits of about 80° C. to about 220° C. and are used in conventional varnish and paint formulations can be used as the solvent in the liquid coating compositions of this invention and as diluents for adjusting the compositions to a desired application consistency. For economical reasons, mineral spirts, V. M. and P. naphtha, and petroleum naphthas are ordinarily preferred over the aromatic solvents such as toluol and xylol. Alcohols, esters, ketones and other conventional volatile compatible organic solvents can be used in admixture with the hydrocarbon solvents where these modifying volatile diluents serve a desirable function. It is preferred that the solvent or diluent be substantially free from water as many of the organic-solvent-soluble titanium derivatives are susceptible to hydrolysis.

For the primary utility of the coating compositions of this invention, the compositions are ordinarily clear unpigmented products. However, for general use the coating compositions can be pigmented with any of the pigments, extenders, fillers, lakes and dyes used in the formulation of conventional varnishes, enamels and paints. These pigmented compositions can ordinarily contain as much as equal amounts by weight of pigment and butadiene polymer binder. Presence of a small amount of zinc oxide pigment is particularly desirable in the coating compositions used to coat containers for pork and corn because it serves as a sequestering agent for sulfur which may be liberated from these processed food products to cause sulfur-staining in the absence of an adequate sequestering agent.

The coating compositions can also advantageously contain still other functional modifiers, such as metal driers which are used in conventional varnishes to control the rate of cure and liquid siloxane polymers which serve to alter the surface characteristics of the applied coating, particularly to improve the wetting of the metal substrate by the liquid coating composition to prevent eye-holing. While for use in interiorly coating of containers, the dry coating preferably consists essentially of the butadiene polymer modified with the effective titanium derivatives, the coating compositions for general utility can also contain compatible resins and plasticizers in minor proportions. The trialkyl orthophosphates, particularly tri-2-ethylhexyl-phosphate, were found to be excellent flexibilizers and when used in the range of about 1% to 5% based on the weight of the butadiene polymer were found to advantageously improve the cure.

In applying the invention compositions to ferrous metal substrates, such as tin-plated sheet steel, sheet steel, terneplate and aluminum clad steel, the coating after substantial volatile loss of solvent is cured by heating the coated substrate preferably at an approximate temperature of 385° F. for a period of 5 to 15 minutes. Other temperatures in the range of 250° F. to 420° F. can be used to equivalently cure the coatings by correspondingly altering the heating or baking period in the range of about 60 to 5 minutes. A curing temperature as low as about 200° F. is operative but a long curing time at this temperature ordinarily is impractical for commercial operations. Use of curing temperatures above 420° F. up to the decomposition temperature does not permit a significant reduction in curing time below the indicated 5 minutes preferred minimum. In the presence of metallic driers, the coatings will air-dry or cure to a tack-free state, but the coatings are preferably cured by baking. Heating can be accomplished by any of the conventional means used in the coating industry.

The liquid coating compositions can be applied by any of the conventional methods employed by the coating industry. However, for coating of sheet metal used in container fabrication, roller coating is a preferred method as the desired coating weight is easily and conveniently applied in a single coat and the liquid coating can be applied at a non-volatile content as high as about 70% by weight. For general coating purposes spraying, dipping and flow-coating are also useful methods of application.

The preferred coating weight for coating ferrous metal sheet substrates with an adequately protective organic coating for use as an interior coating of containers used in the packaging of wet-pack food products is in the range of 2 to 8 milligrams of dry coating per square inch of surface. At coating weights lower than 2 milligrams per square inch the coating ordinarily is not sufficiently protective and not adequately fracture-resistant to either the mechanical operations of container fabrication or the conditions associated with heat-processing food products in direct contact with the coating on the interior surface of the container. No significant advantages are recognized in applying as an interior coating for food containers fabricated from tin-plated sheet steel a coating weight greater than 8 milligrams per square inch of surface. Coating weights greater than 8 milligrams per square inch can be used when the clear or pigmented products serve as a general purpose decorative and protective coating applied either as a single coat or as multiple coats to a ferrous metal substrate. In the general utility of the coatings, they can represent either the entire surface coating on the substrate or at least one layer of a composite surface coating consisting of a plurality of layers. For example, the coating can be applied as the primer coat directly on the substrate and at least one conventional top-coat finish applied thereover or a conventional coating can be used as the undercoat with the invention composition used as the top-coat finish.

While the primary process of the invention relates to precoating a ferrous metal sheet with a coating composition comprising butadiene polymer modified with selected organic derivatives of titanium, and thereafter fabricating the precoated metal as a container, the coating compositions can also be used to interiorly coat containers prefabricated from uncoated metal parts. The coating compositions can also be used as a top-coat over the metal substrate precoated with a primer. When the coating composition is applied to the interior surface of prefabricated metal containers, it ordinarily is applied by spraying.

Use of these modified butadiene polymer coating compositions provide a desirable advance in the art of fabricating interiorly coated metal containers, particularly those containers used in the packaging of wet-pack food products which are heat-processed in the container and aqueous alcoholic beverages which are pasteurized in the container and stored therein for lengthy periods of time. Improved flexibility and superior fracture-resistance of the cured coating on a ferrous sheet metal substrate at a conventional protective coating weight coupled with physical and chemical resistance of the coating to aqueous extracts of wet-pack food products heat-processed in direct contact with the protective organic coating on the interior surface of the container provides an advantageously improved container for the food and beverage canning industry.

While there are disclosed above but a limited number of embodiments of the coating compositions, processes and products of the invention, it is possible to produce still other embodiments without departing from the inventive concept herein disclosed, and it is desired therefore that only such limitations be imposed on the appended claims as are stated therein or required by the prior art.

The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. A coating composition consisting essentially of (A) at least one oily butadiene polymer characterized by an

average molecular weight from about 700 to about 20,000 selected from the class consisting of (1) homopolymers of butadiene-1,3, (2) copolymers of butadiene-1,3 and styrene having at least 75% by weight of copolymerized units of butadiene 1,3 and (3) said homopolymers and said copolymers modified with an anhydride of an unsaturated dicarboxylic acid selected from the class consisting of maleic anhydride and citraconic anhydride in an amount up to 2% based on the weight of said polymers, and (B) at least one substantially non-volatile organic-solvent-soluble organic derivative of titanium selected from the class consisting of (1) orthotitanate esters of aliphatic monohydric alcohols, (2) orthotitanate esters of 2,3 diorgano-substituted 1,3 diols, (3) orthotitanate esters of enolizable beta-ketoacid esters and (4) titanium acylates of fatty oil acids, the proportion of (B) being from about 1% to about 15% based on the weight of said component (A).

2. A liquid coating composition consisting essentially of (A) at least one oily butadiene polymer characterized by an average molecular weight from about 700 to about 20,000 selected from the class consisting of (1) homopolymers of butadiene-1,3, (2) copolymers of butadiene-1,3 and styrene having at least 75% by weight of copolymerized units of butadiene 1,3 and (3) said homopolymers and said copolymers modified with an anhydride of an unsaturated dicarboxylic acid selected from the class consisting of maleic anhydride and citraconic anhydride in an amount up to 2% based on the weight of said polymers, and (B) at least one substantially non-volatile organic-solvent-soluble organic derivative of titanium selected from the class consisting of (1) orthotitanate esters of aliphatic monohydric alcohols, (2) orthotitanate esters of 2,3 diorgano-substituted 1,3 diols, (3) orthotitanate esters of enolizable beta-ketoacid esters and (4) titanium acylates of fatty oil acids, and (C) a volatile liquid organic solvent for (A) and (B) characterized by a boiling temperature from about 80° C. to about 220° F., the proportion of said component (B) being from about 1% to about 15% based on the weight of said component (A) and the total non-volatile content being in the range of about 10% to about 70% based on the total weight of the liquid composition.

3. The coating composition of claim 1 in which (B) the organic derivative of titanium is tetra(2-ethylhexyl) orthotitanate.

4. The coating composition of claim 1 in which (B) the organic derivative of titanium is the orthotitanate ester of 2-ethylhexanediol-1,3.

5. The coating composition of claim 1 in which (B) the organic derivative of titanium is the orthotitanate ester of ethylacetoacetate.

6. The coating composition of claim 1 in which (B) the organic derivative of titanium is polymeric isopropoxy-titanium oleate.

7. The coating composition of claim 1 in which (A) the butadiene polymer is a homopolymer of butadiene-1,3.

8. The coating composition of claim 1 in which (A) the butadiene polymer is a copolymer of butadiene-1,3 and styrene having at least 75% by weight of copolymerized units of butadiene 1,3.

9. The coating composition of claim 1 in which (A) the butadiene polymer is a butadiene homopolymer modified with up to 2% by weight of maleic anhydride.

10. The liquid composition of claim 2 in which said component (C) consists essentially of a hydrocarbon solvent.

11. A process of preparing a liquid coating composition, designed for interiorly coating metal containers used in food processing and packaging, which comprises mixing (A) at least one oily butadiene polymer characterized by an averag meolecular weight from about 700 to about 20,000 selected from the class consisting of (1) homopolymers of butadiene-1,3, (2) copolymers of butadiene-1,3 and styrene having at least 75% by weight of copolymerized units of butadiene 1,3, and (3) said homopolymers and said copolymers modified with an anhydride of an unsaturated dicarboxylic acid selected from the class consisting of maleic anhydride and citraconic anhydride in an amount up to 2% by weight of said polymers, with (B) at least one substantially non-volatile organic-solvent-soluble organic derivative of titanium selected from the class consisting of (1) orthotitanate esters of aliphatic monohydric alcohols, (2) orthotitanate esters of 2,3 diorgano-substituted 1,3 diols, (3) orthotitanate esters of enolizable beta-ketoacid esters and (4) titanium acylates of fatty oil acids, in the presence of (C) a volatile liquid organic solvent for (A) and (B) characterized by a boiling temperature from about 80° C. to about 220° C., the proportion of said component (B) being from about 1% to about 15% based on the weight of said component (A), and the total non-volatile content being in the range of about 10% to about 70% based on the total weight of the liquid composition.

12. A process of preparing a formable organic-coated sheet metal substrate designed for use as a component part of a packaging container which comprises applying to at least one surface of a thin sheet metal substrate a thin coat of the liquid coating composition of claim 2, in an amount corresponding to a dry coating weight of from 2 to about 8 milligrams per square inch of substrate surface, drying said coating by volatile loss of solvent therefrom and curing the resulting coating by heating under conditions corresponding from about 60 minutes at 250° F. to 5 minutes at about 420° F.

13. In the process of manufacturing metal packaging containers involving fabrication of interiorly coated containers from container parts stamped from a ferrous metal sheet precoated with a cured organic coating which shall constitute the interior coating of the container, the improvement which consists of the steps of applying to at least one surface of the metal sheet a sufficient amount of the coating composition of claim 2 to provide a dry coating weight of about 2 to 8 milligrams per square inch of coated surface, drying the coating by partial loss of the volatile organic solvent therefrom, and heating the coated metal sheet at a temperature in the range of about 250° F. to about 420° F. for a period of time ranging from about 60 minutes to about 5 minutes to effect a degree of cure substantially equivalent to heating the coated substrate at 385° F. for 5 to 15 minutes.

14. The improved process of claim 13 in which said coating composition consists essentially of (A) a homopolymer of butadiene-1,3 having a molecular weight in the range of 1000 to 5000, (B) about 1.5% to about 6.0%, based on the weight of (A), of tetra(2-ethylhexyl) orthotitanate, and (C) a volatile hydrocarbon solvent for (A) and (B) having a boiling range within the limits of about 80° C. and about 220° C.

15. A thin formable flat ferrous metal sheet, designed for stamping into precoated container parts, having a baked coating of the product of claim 1 on at least one surface thereof in an amount from 2 to about 8 milligrams per square inch of coated surface.

16. A container comprising a ferrous sheet metal cylindrical body part provided with at least one ferrous sheet metal end-closure sealed to said cylindrical body, the inner surfaces of said container having a baked coating of the product of claim 1 at a dry coating weight of from 2 milligrams to about 8 milligrams per square inch of coated surface.

17. A container comprising a ferrous sheet metal cylindrical body part having a baked coating of the product of claim 1 on the interior surface thereof provided with at least one ferrous sheet metal end-closure sealed thereto, said end-closure having a baked coating of the product of claim 1 on the surface corresponding

to an interior surface of said container, said body part and said end-closure each having said coating at a dry coating weight of from 2 to about 8 milligrams per square inch of coated metal surface, said ferrous metal of said body part and said end closure being tin-plated sheet steel have a coating of tin in an amount of .25 to 1.5 pounds of tin per 218 square feet of surface area of said ferrous metal.

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