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VARNISH PAPER LINER FACING MATERIAL

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This invention relates to a coated paper liner facing material which is suitable for use in contact with foodstuffs for sealing paper, glass and metal containers and which is particularly valuable as a component of crown caps, screw caps and similar closures as a material for resilient discs of cork, cardboard, etc., employed therein, and as a facing material for the inside of paper containers.

Such closures have been made with a resilient disc of cork or cardboard to permit accommodation to all irregularities of the container surface which is to be sealed, but because of the lack of moisture resistance of cardboard and to prevent contamination of the foodstuff by foreign flavors imparted by the cardboard or cork, it is advantageous to employ a protective facing. Various materials have been used heretofore as facings, but none of those used has been satisfactory in all respects. Some have given satisfactory results with a limited number of food products, thus requiring the manufacture and segregation of different types of facings for different food products. For example, relatively expensive aluminum foil has been extensively used as a facing in crown caps for beer, but since aluminum is lacking in resistance to acids such as those contained in citrus products, ginger ale and the like, and to mild alkalis such as those present in certain mineral waters, aluminum foil has attained only limited application as a facing material.

Tin foil has been applied as a facing for closures, especially for the more acid and the more alkaline beverages, but it is more expensive than aluminum and like aluminum tends to contaminate the foodstuff with corrosion products that adversely affect flavor and color of some foodstuffs.

Varnished paper has been employed as a facing for closures and in many respects has superior qualities. It is cheap compared to metal foils and can be made at high speed with great uniformity on comparatively simple roller coater and baking equipment. Varnished paper has excellent moisture resistance and resistance to acids and alkalis of the strengths ordinarily contained in foods, and despite its tendency to impart oily or varnish-like flavors to delicately flavored foods, enjoys very wide application in the closure industry due to its relatively low price. It has been found to be impossible to produce a varnished paper free from this objectionable flavor-imparting characteristic largely because the baking temperature used to cure the varnish

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is limited by the tendency of even the best grades of paper to become brittle at baking oven temperatures. White sulphite papers may not be baked above 300 degrees F. without an appreciable loss in strength, which causes cracking or splitting of the coated paper in the closing or crowning operation. Even the special grades of heat resistant papers such as kraft and Drab Express stock begin to embrittle at baking temperatures slightly in excess of 350 degrees F. Therefore, even the high quality varnishes that produce almost flavor-free films when applied to metal surfaces such as steel, aluminum or tin plate and baked at 400 degrees F., as in the manufacture of metal containers and closures, cannot be made free from off-flavor imparting constituents when coating paper because of this baking temperature limitation.

Still another type of coated paper used as a facing for closures consists of a plasticized film of vinyl chloride-vinyl acetate coploymer calendered to a paper backing with heated rolls. While this type of coated paper has good flavor characteristics, good chemical resistance to a variety of products and fair resistance to moisture and carbon dioxide gas transmission, it is used to a much lesser extent than varnished paper primarily because of its greater cost. The high cost is due in part to the relatively high cost of the vinyl type resins and in part to the fact that the calendering operation, even with the use of the finest types of the very complicated and expensive equipment available for this purpose, cannot produce a uniform and continuous vinyl resin film in thicknesses below 0.002 of an inch. Furthermore, the unmodified vinyl copolymer of, for example, 87 percent vinyl chloride and 13 percent vinyl acetate composition, having a fairly good moisture resistance, cannot be heat-calendered. The addition of a softening agent is also essential to the satisfactory service of the vinyl resin calendered coated paper liner, since in films 0.002 of an inch thick or thicker, the non-softened vinyl copolymer is too hard and unyielding to give a satisfactory seal between the vinyl film and the glass or metal sealing surface of the container. Such softening plasticizers are commonly added in quantities equal to 15 to 20 percent of the resin. The use of softening plasticizers is objectionable in liners for closures for food containers because of their tendency to impart foreign flavors to foods and because plasticizers tend to reduce the general chemical, water and gas resistance of the resin. Also, in times of

national emergency, the few plasticizers that are least objectionable may become unavailable.

It has been discovered that all of the desirable characteristics previously described for varnished paper can be retained and the flavor imparting tendency overcome by applying a thin film of vinyl chloride-vinyl acetate copolymer over a varnished paper base, thus producing a closure facing material superior to any heretofore known to the industry. This desirable result is secured by virtue of the fact that in thin films of the order of one to five ten-thousandths (0.0001 to 0.0005) of an inch thickness (2 to 10 mg. per sq. in.), the vinyl resin has adequate inherent plasticity without the addition of any plasticizer whatever, to give a satisfactory seal between the vinyl film and the sealing surface of the glass or metal container, and in addition this very thin film of vinyl resin completely prevents the transfer to the product of the oily, off-flavor-producing constituents of the varnish film. A film of about 5 milligrams per square inch of surface is presently preferred where the coated paper is non-rigid or where sharp folds and bends are necessary in forming the material or applying the seal.

In the practice of this invention, bleached sulphite paper may be used where whiteness is especially desired, but the more highly heat-resistant kraft papers and particularly the special grade of unsized highly calendered kraft paper made from spruce and known as Drab Express stock is preferred. A paper thickness of four and a half to five thousandths (0.0045 to 0.005) of an inch is preferred when the coated paper is intended for use in crown and screw caps although lighter or heavier gages may obviously be employed for particular purposes. Any sizing upon the paper should not be swellable by water when wet food products or the like are to be contacted, because inferior adhesion of the varnish to the paper stock as well as reduced resistance to moisture vapor penetration would then result.

The chosen paper stock is varnished, for example, by means of the usual roller coating machine, and the varnish is cured in a festoon or a tower-type baking oven. Several different methods of varnishing, as described below, are practiced commercially and any of these may be employed without departing from the principle of this invention, as long as a water- and gas-impermeable varnish film is produced having adequate acid and alkali resistance to permit its use in contact with beverages, other foods and certain industrial products.

Three methods of varnishing that may be employed are as follows:

1. Stop Coat Method

One side of the paper is roller coated with an oleoresinous varnish having a relatively high viscosity so that only enough penetration of the varnish into the paper fibers occurs to provide a strong adhesive bond. The wet varnished paper web passes into a drying oven where the high-temperature-induced oxidation and polymerization cause the oleoresinous varnish film to become hard and tack-free. A second coat of varnish is then applied to the same side of the paper and baked in the same manner. Stop coat methods permit use of higher resin:oil ratios than saturating methods, since the coating does not produce brittleness to the extent of such saturating coatings; and the stop coating penetrates into the paper base only to the extent necessary to obtain strong adhesion to the paper.

2. Saturating Method

One side of the paper is roller coated with an oleoresinous varnish at a somewhat lower viscosity than in the stop coat method so that the paper becomes completely saturated with the varnish. After passing through the baking oven, the saturated paper is varnished a second time on the same side of the paper, and re-baked.

3. Simultaneous Two Side Method

In this method of varnishing, the paper is dipped in or passed through a saturating or stop coat type oleoresinous varnish so that both sides of the paper are coated simultaneously. After passing through the baking oven, the two-side varnished paper is varnished a second time as before, and re-baked.

The preferred thickness of the double coating of oleoresinous varnish, upon the paper, is from 20 to 40 milligrams per square inch.

Satisfactory varnishes for producing the desired water, water vapor and gas impermeable varnished paper may be produced from various drying oils in combination separately with various types of compatible resins, and having various proportions of resin to drying oil. The drying oils preferred in the order of their suitability are tung oil, dehydrated castor oil and alkali-isomerized linseed oil. Resins capable of increasing the hardness, water and chemical resistance of these oils include, but are not limited to, phenolic (phenol-aldehyde) resins, modified phenolic resins, fossil gums and maleic-anhydride glycerol esters of rosin.

Examples of oleoresinous varnishes suitable for these methods of application are as follows:

Saturating Varnishes

Example No. 1

	Pounds
Phenolic resin (Bakelite BR-254)	100
Tung oil	400
Manganese resinate	4
Xylol	1175

Example No. 2

	Pounds
Modified phenolic resin (M-86)	100
Dehydrated castor oil	400
Manganese resinate	4
Xylol	1175

Example No. 3

	Pounds
Modified maleic resin (Amberol 809)	100
Isomerized linseed oil (Kellimol)	400
Manganese resinate	4
Xylol	1175

Stop Coat Varnishes

Example No. 4

	Pounds
Phenolic resin (Bakelite BR-254)	100
Tung oil	420
Manganese resinate	1.5
Xylol	330

Example No. 5

	Pounds
Modified phenolic resin (M-86)	100
Dehydrated castor oil	100
Manganese resinate	1
Xylol	200

The manganese resinate is a drier, and may be omitted or replaced by another drier, depending

upon this drying capability of the oleoresin and the availability of the drying agents. The xylol is an organic solvent volatile below the baking temperature, and may be replaced by other volatile solvents.

To the completely varnished paper which has a film weight of baked oleoresinous varnish of 20 to 40 milligrams per square inch of surface and, except for its flavor-imparting characteristics, has all of the qualities required of a high quality cap liner, is then applied, e. g., by means of a roller coating machine, a very thin film of vinyl resin lacquer which is singularly effective in preventing the transmission of the oily and varnish-like flavors to the food product.

The vinyl resin lacquer should be applied to produce, after baking, a dry film weight of 2 to 10 milligrams per square inch of surface which, depending upon the exact type of vinyl resin chosen and the accompanying modifiers, is equivalent to a film thickness of about one to five ten-thousandths (0.0001 to 0.0005) of an inch. Thinner vinyl resin films are not completely effective in sealing off the oily and varnish-like flavors, while films thicker than five ten-thousandths (0.0005) of an inch, in the absence of plasticizer, begin to show poorer gas pressure sealing efficiency due to their stiffness and inability to conform to imperfections in the container sealing surface. In addition, no advantage is gained by using quantities of the relatively expensive vinyl resins in thicknesses greater than five ten-thousandths (0.0005) of an inch, which has been found to provide entirely adequate flavor protection.

The term "vinyl resin" includes those resins produced by the polymerization of compounds containing the vinyl or vinylidene group, more particularly the resins manufactured from vinyl and vinylidene halides and mixtures thereof with vinyl esters, and with acrylic acids and their esters, such as the conjoint interpolymers of the type containing 60 to 95 percent of vinyl chloride and 40 to 5 percent of vinyl acetate, or similar proportions of vinyl or vinylidene halide with other vinyl esters, acrylic acid, alkacrylic acid, acrylic and alkacrylic esters. In order to obtain a high resistance to reaction with or transmission of water, the vinyl resin should have a high vinyl halide content. The commercially available resin, known as Vinylite VYHH (a copolymer from about 87 percent of vinyl chloride and 13 percent of vinyl acetate) is the presently preferred resin for practicing this invention.

The following formula is an example of a suitable lacquer composition:

Example No. 6

	Pounds
Vinyl chloride-acetate polymer resin (Vinylite VYHH)	17.0
Methyl ethyl ketone	37.35
Toluol	37.35
Methyl isobutyl ketone	8.3
	100.00

In order to reduce the materials cost, obtain improved adhesion to the oleoresinous base coat, and secure increased resistance to water vapor or carbon dioxide gas penetration, a portion of from 5 to 15 percent of the vinyl resin may be replaced with a flexible compatible resin of a different type which itself is highly resistant and gives no off-flavors after baking at temperatures below 350 degrees F. The most suitable modifying resins for this purpose are the maleic-anhydride glycerol esters of rosin which are available from various resin suppliers under trade names such as Beckacite 1111, Amberols 800 and 801, and Syntex H-3.

A specific illustration of this type of modification follows:

Example No. 7

	Pounds
Vinyl chloride-acetate polymer resin	15.3
Maleic anhydride glycerol rosin esters	1.7
Methyl ethyl ketone	37.35
Methyl isobutyl ketone	8.3
Toluol	37.35
	100.00

In the event that extremely high holding power against carbon dioxide gas pressure is required, as when carbonated-type beverages are to be sealed, up to 10 percent of the weight of the vinyl resin may be replaced with a compatible, non-toxic, flavor-free high-boiling and non-water-reactive modifying agent such as dibutyl Cellosolve phthalate, methyl phthalyl, ethyl glycollate, or diamyl phthalate. Two examples of this type of formulation are:

Example No. 8

	Pounds
Vinyl chloride-acetate polymer resin	16.25
Methyl phthalyl ethyl glycollate	.75
Methyl isobutyl ketone	8.3
Toluol	37.35
Methyl ethyl ketone	37.35
	100.00

Example No. 9

	Pounds
Vinyl chloride-acetate polymer resin	16.25
Dibutyl Cellosolve phthalate	0.75
Methyl ethyl ketone	37.35
Methyl isobutyl ketone	8.3
Toluol	37.35
	100.00

For certain applications where the typical yellow-brown varnish color is undesirable, the appearance of the coated paper may be enhanced by the addition of suitable pigments. White and aluminum pigments are particularly advantageous. Typical examples of these are:

Example No. 10

	Pounds
Titanium dioxide pigment	7.14
Vinyl chloride-acetate polymer resin	15.00
Diamyl phthalate	1.66
Methyl isobutyl ketone	7.62
Methyl ethyl ketone	34.29
Toluol	34.29
	100.00

Example No. 11

	Pounds
Aluminum powder	1.19
Vinyl chloride-acetate polymer resin	15.31
Methyl isobutyl ketone	8.30
Methyl ethyl ketone	37.35
Toluol	37.35
	100.00

The ketones and toluol in the examples provide an organic solvent for the vinyl resin, and for the modifying agent where employed; and may

be replaced by another organic solvent which is volatile below the baking temperature for the vinyl resin film, i. e., about 300 degrees F. The proportions may be varied in accordance with the selected method of application, the stated proportions being desirable for compositions which may be stored before use.

It has been found that a desirable improvement in adhesion to the varnish of the vinyl resin film, with exhibition of good chemical and physical properties even when all the solvent has not been eliminated, can be secured by the addition of a tripolymer resin containing maleic anhydride, vinyl chloride and vinyl acetate, such as that which is commercially available under the designation Vinylite VMCH, which contains approximately 2 parts of maleic component copolymerized with about 87 parts of vinyl chloride and 13 parts of vinyl acetate. Tests have shown that a replacement of 20 percent of the vinyl chloride-vinyl acetate resin by such a tripolymer, as exemplified by the following formula, is to be preferred although considerable deviations from this basic formula can be made.

Example No. 12

	Pounds
Vinyl chloride-acetate polymer resin	13.6
Tripolymer resin from maleic anhydride, vinyl chloride and vinyl acetate (Vinylite VMCH)	3.4
Methyl isobutyl ketone	8.3
Methyl ethyl ketone	37.35
Toluol	37.35
	100.00

In baking the vinyl resin top coat a minimum temperature of 285 degrees F. is required to release the solvents and to develop satisfactory adhesion of the top coat to the underlying oleoresinous varnish. A maximum baking temperature limitation is set by the tendency of vinyl resins to decompose at higher temperatures; however, it has been determined that the practical maximum is fixed by the tendency of the preferred paper base to become embrittled at temperatures exceeding 350 degrees F. Within the range of 300 to 350 degrees F., elimination of solvent from the vinyl resin and the development of adequate adhesion to the varnish are accomplished.

As a specific example of the practice of this invention, a Drab Express paper was stop-coat-varnished with a dehydrated castor oil varnish (Example No. 2 above) and baked at 350 degrees F. for 40 minutes. The resulting paper had a very high moisture-vapor permeability and therefore was unsuited for use as a cap liner. A second coat of varnish was applied and baked at 350 degrees F. for 40 minutes. The double-coated paper then had a sufficiently low moisture vapor transmission value as shown in Table I below but, when tested in a crown cap in contact with beer for ten days, transmitted to the beverage an objectionable oily flavor. Two portions of the same lot of double varnished paper were re-lacquered with a vinyl resin lacquer (Example No. 6 above) in thicknesses of deposit which produced, after baking at 300 degrees F. for 3 minutes, dry film weights of vinyl resin of two and of five milligrams per square inch of surface, respectively. These triple coated papers, as indicated in Table I, had even lower moisture vapor transmission values and when flavor-tested with beer, were found to impart no foreign flavors whatever to the beverage.

Table I

	Moisture vapor transmission [1] gms./100 sq. inches/24 hours
Drab Express paper with stop coat and top coat of dehydrated castor oil varnish	5.00
Drab Express paper with stop coat and top coat of dehydrated castor oil varnish, plus a 2 mg./sq. in. coat of vinyl resin	3.11
Drab Express paper with stop coat and top coat of dehydrated castor oil varnish, plus a 5 mg./sq. in. coat of vinyl resin	1.91
Calendered Vinylite coated paper	3.91

[1] At 98 degrees F. with anhydrous calcium chloride on one side of film, 95 percent humidity on other.

As another specific example, a Drab Express paper was coated with a stop coat and a top coat of a tung oil varnish (Example No. 1 above) and baked for 40 minutes at 350 degrees F. following each application. As shown in Table II below, the double varnished paper had a lower moisture-vapor transmission value than the above calendered Vinylite coated paper and hence in this respect, at least, was superior to the latter. However, when crown caps having a 0.85 inch diameter circular spot facing of this varnished paper adhered to the cork were tested in contact with beer, a faint but unmistakable oily flavor was discerned in the beverage by expert taste testers. This off-flavor was less objectionable than in the case of the dehydrated castor oil varnished paper heretofore described, but was sufficiently noticeable to prevent the utilization of the tung oil varnished paper for this purpose.

A quantity of the same double-varnished paper was re-lacquered with a vinyl resin lacquer (Example No. 6 above) producing after a three minute bake at 300 degrees F., a dry vinyl lacquer film weight of 5 mg./sq. in. The completed paper showed only a very slightly greater resistance to moisture-vapor transmission, but expert flavor testers pronounced the triple coated paper perfectly free from foreign flavor imparting characteristics after a prolonged storage period in contact with beer, thus proving that the thin coat of vinyl resin acts as an impermeable membrane to the off-flavor imparting components of the varnish film.

Table II

	Moisture water transmission [2] gms./100 sq. inches/24 hours
Drab Express paper with a stop coat and a top coat of tung oil varnish	3.00
Drab Express paper with a stop coat and a top coat of tung oil varnish, plus a 5 mg./sq. in. coat of vinyl resin	2.88

[2] At 98 degrees F. with anhydrous calcium chloride on one side of film, 95 percent humidity on other.

The completed vinyl resin coated varnished paper produced according to this invention may be fabricated in the usual ways, without any special requirements or limitations. For example, it may be laminated to cardboard or other backing material, punched into discs and inserted in caps on a single machine such as is used in the industry, or the discs cut with a simple die may be inserted by hand or by any other convenient means.

For use with cork in crown caps, it is perfectly feasible to apply a thermoplastic cement to the reverse side of the paper and to cut discs of the desired diameter, which may be somewhat less than the diameter of the cork liner, and to insert and adhere the coated paper spot to the cork on one of the special machines employed for this

purpose. Suitable adhesives are gutta percha and alkyd resin base thermoplastic adhesives.

It is obvious that the invention may be employed in many ways within the scope of the appended claims.

I claim:

1. A paper liner facing material comprising a paper base and a coating thereon comprising a paper-adherent layer of oleoresinous varnish sealing the paper base and providing a continuous outward surface, and a continuous top coating film having an unplasticized resinous base consisting for 80 to 100 percent by dry weight of vinyl polymer resin selected from the group consisting of polymerized vinyl and vinylidene halides and vinyl resins containing 40 to 95 percent by weight of vinyl and vinylidene halides as mixed and interpolymers with vinyl esters, acrylic acid, esters of acrylic acid, and alkyl-substituted acrylic acids and their esters; the remainder of the dry weight of the resin base of said top coating film being a resin selected from the group consisting of maleic anhydride glycerol esters of rosin and the tripolymer resin made from maleic anhydride, vinyl halide and vinyl acetate; said top coating film being adherent to said oleoresinous layer and having a thickness of substantially one to five ten-thousandths of an inch with a dry film weight of substantially 2 to 10 milligrams per square inch, said material being characterized by being flexible, having a tough and impermeable exposed surface and having its several components inseparably bound together.

2. A paper liner facing material comprising a paper base and a coating thereon comprising a paper-adherent layer of oleoresinous varnish sealing the paper base and providing a continuous outward surface, and a continuous top coating film having an unplasticized resinous base of which for 80 to 100 percent by dry weight consists of vinyl resin which is a copolymer of approximately 87 percent vinyl chloride and 13 percent vinyl acetate, said top coating film being adherent to said oleoresinous layer and having a thickness of substantially one to five ten-thousandths of an inch with a dry film weight of substantially 2 to 10 milligrams per square inch, said material being characterized by being flexible, having a tough and impermeable exposed surface and having its several components inseparably bound together.

3. A paper liner facing material comprising a paper base and a coating thereon comprising a paper-adherent layer of oleoresinous varnish sealing the paper base and providing a continuous outward surface, and a continuous top coating film having a plasticized resin base consisting essentially of a mixture containing 80 percent by dry weight of copolymer of vinyl chloride and vinyl acetate with the ratio of the vinyl chloride component to the vinyl acetate component being from 60:40 to 95:5; the the remainder of said top coating film mixture being a tripolymer formed from substantially 2 parts by weight of maleic anhydride, substantially 87 parts of vinyl chloride and 13 parts of vinyl acetate, being compatible with the said copolymer vinyl resin and free from off-flavor when baked therewith at a temperature between 285 and 350 degrees F.; said top coating film being adherent to said oleoresinous layer and having a thickness of substantially one to five ten-thousandths of an inch with a dry film weight of substantially 2 to 10 milligrams per square inch; said material being characterized by being flexible, having a tough and impermeable exposed surface and having its several components inseparably bound together.

4. A paper liner facing material comprising a paper base and a coating thereon comprising a paper-adherent layer of oleoresinous varnish sealing the paper base and providing a continuous outward surface, and a continuous top coating film having a resin base consisting essentially of a mixture containing 85 to 95 parts by dry weight of copolymer of vinyl chloride and vinyl acetate with the ratio of the vinyl chloride component to the vinyl acetate component being from 60:40 to 95:5; the remainder of the said top coating film mixture being 5 to 15 parts of maleic anhydride-glycerol ester of rosin, being compatible with the said copolymer vinyl resin and free from off-flavor when baked therewith at a temperature between 285 and 350 degrees F.; said top coating film being adherent to said oleoresinous layer and having a thickness of substantially one to five ten-thousandths of an inch with a dry film weight of substantially 2 to 10 milligrams per square inch; said material being characterized by being flexible, having a tough and impermeable exposed surface and having its several components inseparably bound together.

5. A paper liner facing material comprising a paper base and a coating thereon comprising a paper-adherent layer of oleoresinous varnish sealing the paper base and providing a continuous outward surface, and a continuous top coating film having a thickness of substantially one to five ten-thousandths of an inch with a dry film weight of substantially 2 to 10 milligrams per square inch; said top coating film having an unplasticized resin base adherent to said oleoresinous layer, with said resin base consisting of at least 80 percent dry weight of a vinyl polymer resin selected from the group consisting of polymerized vinyl and vinylidene halides and vinyl resins containing 40 to 95 percent by weight of vinyl and vinylidene halides as mixed and interpolymers with vinyl esters, acrylic acid, esters of acrylic acid, and alkyl-substituted acrylic acids and their esters; the remainder of the dry weight of the resin base of said top coating film being a resin selected from the group consisting of maleic anhydride glycerol esters of rosin and the tripolymer resin made from maleic anhydride, vinyl halide and vinyl acetate; said material being characterized by being flexible, having a tough and impermeable exposed surface and having its several components inseparably bound together.

6. A paper liner facing material comprising a paper base and a coating thereon comprising a paper-adherent layer of oleoresinous varnish sealing the paper base and providing a continuous outward surface, and a continuous top coating film having a thickness of substantially one to five ten-thousandths of an inch with a dry film weight of substantially 2 to 10 milligrams per square inch; said top coating film having an unplasticized resin base adherent to said oleoresinous layer, with said resin base consisting of unplasticized vinyl polymer resin which is a copolymer of approximately 87 percent of vinyl chloride and 13 percent of vinyl acetate; said material being characterized by being flexible, having a tough and impermeable exposed surface and having its several components inseparably bound together.

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