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AQUEOUS COATING COMPOSITION CONTAINING STYRENE-BUTADIENE COPOLYMER AND POLYETHYLENE, PROCESS OF COATING PAPER THEREWITH AND COATED ARTICLE

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This invention relates to coatings for paper and more particularly to coated containers such as drinking cups, milk cartons and the like used for receiving various foods and beverages, and method of coating the same. The present application is a continuation in part of our co-pending application for patent Serial No. 631,060, filed December 28, 1956.

Uncoated paper tends to become soggy when exposed to water and to noticeably stain when brought into temporary contact with various foods and/or liquids including coffee, tea, cocoa, milk, fruit juices and the like. Drinking cups which stain and show rings are distasteful to many users. Where the containers are to be used for hot beverages such as tea or coffee, protection of the paper by means of a coating is even more important since hot foods tend to disintegrate the paper and to stain it more readily than do cold liquids.

While a number of different materials have been used for coating paper, none have been completely satisfactory from the point of view of providing a waterproof stain resistant coating for containers in which various foods and beverages might be placed. Two of the more commonly used materials have been vinyl chloride-vinyl acetate copolymer solutions and various blends and formulations of paraffin wax. The vinyl copolymers are usually embodied in a volatile organic solvent which can be evaporated to leave a thin coating of the vinyl copolymer on the paper. However, the ordinarily used solvents such as the ketones and esters are inflammable and thus present a fire hazard. Also the characteristic odors of the ketones and esters in which such resins are dissolved are both irritating and present a health hazard to workers coating containers therewith. Further, because it is almost impossible to completely remove all trace of solvent from the coating, a residual odor is left in the coated container which is highly unsatisfactory to those using such coated cups for drinking beverages and the like. Moreover, the organic solvents are relatively expensive, particularly when compared to water.

The various known paraffine wax formulations previously used for coating containers also have their drawbacks. The wax not only has a tendency to flake and crumble from the paper but, in so doing, leaves flakes in the foods and beverage which are distasteful to most users. The wax also provides a taste which is annoying to some users. Moreover, paraffine wax formulations are generally applied hot and require special equipment with resultant high application costs. In the molten state, paraffine definitely presents a fire hazard. Likewise, it is well known that the paraffine wax, because of its low melting point, is not suitable for coating cups or other containers designed to withstand heat as encountered in hot coffee or tea. Such paraffine wax formulations also are ordinarily somewhat opaque, particularly when in heavy films, and so are readily visible when applied over printing as on milk cartons, for example.

Thus a first and principal object of the present invention is to provide a coating for paper and/or coated paper containers that will provide the desired water-proofing and stain resisting characteristics while avoiding or over-

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coming the disadvantages above mentioned for previously available coating materials.

Another important object of the present invention is to provide a coating for paper and/or paper containers which will afford not only a measure of protection to the paper against disintegration and/or staining when brought into contact with hot fluids but will also have the added function of reducing heat transfer through the cup so as to provide a cup or container which can be held more comfortably in the fingers when filled with the hot liquid.

A further object of the invention is to provide such a coating which will not only increase the waterproofness of the paper but will also tend to eliminate the slight characteristic flavor of paper while at the same time itself being substantially free of odor and taste.

A further object of the invention is to provide a coating that will be not only relatively stable and unaffected by various foods and beverages placed in the containers but will also be substantially non-blocking. By non-blocking is meant that when the containers are stacked one within the other they will not tend to stick or join together but may be readily separated and without injuring the coating. The advantages thereof will be readily apparent.

A further object of the invention is to provide a coating which will not only provide the desired waterproofing and stain resistance to the coated paper but will also supply a stiffening or reinforcing action on the paper when formed into a container such as a cup so as to provide strength and thereby increasing its utility while at the same time making it possible to employ paper stock of lighter weight so as to result in significant savings in cost of materials.

In obtaining these objects and others, it is proposed according to the present invention to coat paper and/or paper containers and the like from an aqueous emulsion of resin solids which will provide on evaporation of the water and fusion of the remaining resin solids, a thin continuous film affording the desired resistance to water and staining.

As discussed above, those coatings previously available and used on paper containers ordinarily employed inflammable solvents in which the resin or other coating material was dissolved or dispersed and were therefore hazardous to use not only for health reasons but because of the danger of fire during the coating operation from sparks, static electricity, carelessly thrown matches, cigarettes and the like. Thus it is an important feature of the invention that the paper coating material is contained in a non-inflammable and inexpensive volatile vehicle, namely water.

Another advantage to be gained by the use of water as the volatile vehicle in which the coating material is dispersed is that the water in and of itself possesses no odor or taste. Therefore, where small residual traces of solvent remain in the coating, no persisting characteristic odor or taste remains to affect the beverage or other food placed in the coated container.

In some coating applications, particularly, for example, in forming milk cartons it is desirable to pre-coat the paper and then fold to shape. In this connection, a further object of the invention is to provide a means and method of coating to produce a film having all of the aforesaid advantages and features and which will additionally be sufficiently flexible as not to crack, flake or readily separate from the paper when it is folded.

A further object is to provide such a coating or film on paper which will also seal or fuse on the application of suitable heat and pressure to permit a water tight joint between portions of the paper when folded and brought together to form a container.

A further object of the invention is to provide a coating which on evaporation of the volatile constituent will form a thin continuous film of material having the aforesaid characteristic and which will strongly adhere to the surface of the paper but will not deeply impregnate the paper whereby the desired protection may be obtained using a minimum amount of coating material.

Likewise it is an object of the invention to provide such a coating which will have little or no tendency to flake or peel and will be relatively flexible so that the coating will be useful for providing desired waterproofing and stain resistance to paper when either applied to finished products such as a drinking cup or carton or when applied to paper which is to be subsequently shaped into a container.

Many other objects and advantages as well as features of a coating material, the coated article and method of coating, according to the present invention, are or will become obvious to those skilled from the description thereof which is to follow.

Thus, in accomplishing the aforesaid objects, the inventors have found that a water emulsion of resin solids consisting essentially of polymeric material from the group consisting of (a) water emulsified styrene-butadiene copolymer alone or (b) water emulsified styrene-butadiene copolymer in admixture with water emulsified polystyrene may be prepared. When small amounts of water emulsified polyethylene are mixed therewith, a coating composition is produced which can be conveniently and simply applied to paper, existing either in sheet stock form or in the form of a cup, a carton, a plate or other container so as to obtain, on evaporation of the water, a thin, transparent, continuous film of resin having marked resistance to water penetration and staining by a variety of hot or cold liquids such as the aforementioned milk, coffee, tea, cocoa and fruit juices in addition to a variety of other foods. Such films have been found to be substantially tasteless and odorfree as well as masking the taste of the paper on which the film is applied and imparting insulating qualities against heat.

Although the proportions of the several ingredients may be varied within relatively wide limits, as for example, the proportion of butadiene may range from a minimum of 1% to a maximum of 50% by weight of the total resin, a more satisfactory working range has proved to be obtained wherein the butadiene content is kept between 15 and 25%, with the preferred ratio being near 20 parts by weight of the butadiene moieties per 80 parts of the styrene moieties of the resin content. The polyethylene content we have found is preferably kept in the range of one or two percent; although amounts as high as 3.32% can be added without producing an objectionable browning of the film. A particularly useful proportion we have found comprises about 1.5%.

The resins may be prepared by polymerization in an emulsified state or by emulsification of resins prepared by other methods as widely described in the literature. Ordinarily, it is preferable that the polyethylene be separately emulsified and then added to an emulsion consisting of the aqueous emulsified polystyrene and/or aqueous emulsified styrene-butadiene copolymer. The proportions of water embodied in the emulsion can vary considerably, depending on the viscosity required for the particular method by which the coating is to be applied. Generally speaking, however, emulsions according to the present invention will comprise roughly 25 to 50% by weight of resin solids, the balance comprising water and including a small quantity of suitable emulsifying agent.

Although the coating material may be applied in any one of several ways as by dipping, spraying or flushing, containers such as coffee cups are conveniently coated by using a pair of jets one directed to focus a spray of the coating material onto the inner walls of the cup and a second jet located to direct coating material toward the bottom of the cup so as to completely cover the interior

of the cup, including the rim if desired. It has been found that, although the water in which the resins are contained, will readily penetrate the paper stock, the resin solids do not as readily penetrate and, instead, remains essentially on the surface of the paper as a thin layer which fuses, when heated, into a thin, clear transparent continuous film strongly bonded to the paper surface. This may be accomplished for example by air-drying the coated paper stock or cups for about 10 minutes and then baking at 300° F. for two minutes. However, a preferred method for rapidly removing the water from the film and fusing the resin solids into a continuous film comprises directing air heated to a temperature in the vicinity of 250° F. onto the coated interior of the cups for roughly 1 minute or a time interval sufficient to drive out the water without raising or otherwise blistering the remaining film of resin. The temperature of the thus directed air is then gradually increased over a period of roughly two minutes until it reaches a temperature between 350° and 400° F., at which temperature it is held for approximately 20 seconds or sufficient to fuse the coating into a continuous film providing the desired waterproofing and stain-resisting characteristics. The baking step is then followed by blowing air maintained at room temperature, or slightly below, onto the coated interior of the cups for approximately 30 seconds to cool and otherwise set the film so that there is no problem of the cups sticking when stacked or nested one within the other. The aforesaid time cycle will vary somewhat with the size of the container being coated and/or thickness of the coating.

When coating flat paper stock, preferably the paper, as it leaves the roll, is passed through a bath of the coating material and between wiping blades or a knife as is known to those skilled in the art. Thereafter, the coated paper is subjected to air initially heated to 250° F. as before and which is gradually raised to the mentioned fusing temperature to near 400° F. The coated stock is then cooled to near room temperature.

Where the coating is being used on containers for food or beverages, it is a prime requisite of the selected plasticizer that it be odor and taste free as well as stable. In addition to possessing these properties butadiene is compatible with the polystyrene and/or when in copolymerization with styrene moieties, it has no tendency to leach out or migrate from the film. Its other good film forming properties, plus its low cost, make it the plasticizer of preference.

Although an emulsion of polystyrene and styrene-butadiene copolymer or a styrene-butadiene copolymer resin used alone as the coating material will provide the major proportion of the protection and masking properties desired in the film, we have found that the addition of emulsified polyethylene in the indicated small amounts has the surprising and unexpected result of materially increasing the flow and other film forming characteristics of the resin and particularly the non-blocking and non-melting characteristics of the fused film. Although the proportion of polyethylene resin that may be added can be increased beyond the aforementioned 3.32% by weight of the total resin solids, if necessary to satisfy particular requirements of a specific coating, when polyethylene is present in large proportions, it tends to interrupt the continuity of the fused film. In our coatings the amounts of polyethylene present is sufficiently low that the polyethylene particles are distributed through the film so as not to interrupt the continuity of the film but are effectively surrounded by the polystyrene and/or styrene-butadiene copolymer as to be confined thereby and available for imparting non-blocking properties to the film. We have also noted that when the film contains polyethylene in amounts higher than 3.32% there is a noticeable browning of the film. Since the film has its most important utility as a coating for the interior of coffee cups, such a color might be suggestive of a coffee-stained cup or at least one that is unclean. Therefore we find it important to keep the

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polyethylene content below said maximum. At the same time we have found it desirable to add as much polyethylene to the extent possible without introducing said browning or dark color to the film to obtain maximum non-blocking properties. We have found, however, that useful non-blocking properties can be imparted to the film when the polyethylene content is as low as .625%. With lower proportions of polyethylene there is a proportionate falling off in non-blocking properties imparted to the films. Films comprised entirely of butadiene and styrene moieties show definite signs of blocking.

Although the coating as aforesaid is not particularly effective as a coating for containers in which salad oils or other materials containing large amounts of oils or greases are to be placed, the resistance of the coating to such oils and greases can be improved by the addition of polyacrylic resins to the emulsion. The addition of the polyacrylics also appears to improve the non-wicking properties of the coating so that there is less penetration of the resin film into the paper.

Also if desired, coating compositions may be modified by the addition of polyvinyl resins. These provide a tougher and more flexible film on evaporation of the water. Thus, for example, where the coating material is to be applied to sheet stock which is to be later shaped into a container or other article, films modified with polyvinyl resin will have greater resistance to cracking during the necessary manipulation and/or bending and shaping of the coated paper. The polyvinyl resins also help to increase resistance of the films to attack by oils and greases. Likewise, the films may be modified by the addition of copolymers of styrene and natural or synthetic alcohol soluble resin as, for example: styrene-shellac copolymer, styrene-manila gum copolymer, styrene-maleic copolymer resins, and styrene-allyl starch. These may be added to the coating emulsion to reduce tack, provide better leveling and more uniformly thin continuous films.

There follow typical examples of suitable coating compositions which may be formed and used in accordance with the present invention. In these examples, commercially available emulsions of styrene-butadiene resin copolymers have been modified by the additions of aqueous emulsions of polystyrene alone to obtain the required ratio of styrene moieties to butadiene moieties. The modifying resins are also added as aqueous emulsions and where necessary soft water has been added to obtain the required dilution or viscosity. Thus, in the following examples, "Pliolite 170" is an aqueous emulsion containing about 48% of styrene-butadiene resin in the ratio of 70 parts styrene to 30 parts by weight of butadiene sold by the Goodyear Tire and Rubber Company. The Dow Chemical Company provides under its code 762W an aqueous emulsion containing 48% of resin in the ratio of 33 parts butadiene to 67 parts of styrene by weight. The latter also provides a second aqueous emulsion under the code X2527.4 embodying 48% resin in the ratio of 40 parts by weight of butadiene to 60 parts styrene. These are diluted with polystyrene resin emulsions such as U2001 which is an aqueous emulsion of polystyrene sold by UBS Chemical Company containing approximately 35% of polystyrene resins or that sold by Monsanto Company under code 615 containing approximately 49% of polystyrene resin in an aqueous emulsion.

Preferably, as aforesaid, the polyethylene is separately emulsified, and then added to the polystyrene, styrene-butadiene copolymer emulsion. In the following examples, the polyethylene emulsion referred to was obtained by heating 81 parts of an emulsifiable grade of polyethylene at approximately 250° F. until in a liquid stage, then adding in succession 17 parts of oleic acid and 17 parts of morpholine as an emulsifying agent, the temperature being held at 225 to 235° F. After 2 to 5 minutes, 400 parts of water was gradually added with agitation until the desired emulsion was obtained.

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Example I

A typical all-purpose formula particularly useful in coating containers to be used for drinking cups to contain hot beverages, such as coffee or tea, would comprise:

	Gallons
Styrene-butadiene copolymer emulsion (762W)-----	44
Polystyrene resin emulsion (U2001)-----	32
Polyethylene emulsion-----	4
Deionized water (soft water)-----	20
	100

Example II

A composition having much less wicking and less odor will comprise:

	Gallons
Styrene-butadiene copolymer Emulsion (Pliolite 170) -----	55
Polystyrene emulsion (U2001)-----	40
Polyethylene emulsion-----	5
	100

Example III

Another useful composition that may be formed will comprise:

	Gallons
Styrene-butadiene copolymer emulsion (762W)-----	34
Polystyrene emulsion (615)-----	34
Polystyrene emulsion (U2001)-----	17
Polyethylene emulsion-----	8
Soft water-----	7
	100

Example IV

The increased butadiene content of the following composition permits a much lower fusing temperature.

	Gallons
Styrene-butadiene copolymer emulsion (X2527.4)-----	36.25
Polystyrene emulsion (U2001)-----	18.50
Polystyrene emulsion (615)-----	36.25
Polyethylene emulsion-----	9.00
	100.00

Example V

The following composition is particularly colorless.

	Gallons
Styrene-butadiene copolymer emulsion (762W)-----	55
Polystyrene emulsion (615)-----	40
Polyethylene emulsion-----	5
	100

Example VI

By reason of the higher polyethylene content in this particular composition better blocking resistance is obtained than in the previous example.

	Gallons
Styrene-butadiene copolymer emulsion (762W)-----	49.00
Polystyrene emulsion (615)-----	35.25
Polyethylene emulsion-----	8.75
Soft water-----	7.00
	100.00

Example VII

The composition of the following is particularly useful for coating small cups and the like containers al-

though it has somewhat lower resistance to grease than does the composition of Example I.

	Gallons
Styrene-butadiene copolymer emulsion (762W)---	36.5
Polystyrene emulsion (U2001)-----	18.0
Polystyrene emulsion (615)-----	36.5
Polyethylene emulsion-----	9.0
	100.0

Example VIII

The following is an example of a coating composition which has been found particularly useful in dip application as where sheet stock is being coated.

	Gallons
Styrene - butadiene copolymer emulsion (Pliolite 170)-----	33
Polyacrylic resin emulsion (Rohm & Haas X-52)---	33
Polyethylene emulsion-----	5
Water (demineralized)-----	29
	100

Thus it will be apparent from the above description that all of the objects and advantages of the invention have been demonstrated as obtainable in a convenient, simple, and practical manner.

Thus having described our invention we claim:

1. Paper coated with a baked-on, clear transparent, continuous film deposited from a water emulsion of polymeric material from the group consisting of (a) styrene-butadiene copolymer and (b) mixture of polystyrene and styrene-butadiene copolymer, wherein the styrene moieties of said polymeric material comprise the major portion thereof and the butadiene moieties comprise the minor portion thereof, said film further containing an amount between about .625% and 3.32% by weight of polyethylene uniformly distributed through said polymeric material sufficient to impart non-blocking characteristics to the film without interrupting the continuity of the film and its clear transparent character, said film strongly adhering to the surface of the paper but not deeply impregnating the paper, and said filmed paper possessing heat-insulating as well as non-blocking characteristics and improved resistance to penetration, staining and disintegration of the paper by hot and cold beverages such as coffee, tea, milk, cocoa and fruit juices, said film further being essentially free of taste and odor while tending to mask the taste of the paper over which it is coated.

2. Paper surface-coated with a continuous transparent, adherent heat-fused film from a water emulsion of resin solids consisting essentially of polymeric material from the group consisting of (a) water emulsified styrene-butadiene copolymer and (b) water emulsified polystyrene in admixture with water emulsified styrene-butadiene copolymer, the butadiene moieties of said polymeric material comprising from 15 to 25% by weight and the styrene moieties comprising the balance of said polymeric material, said solids further including an amount between about .625% and 3.32% by weight of water emulsified polyethylene uniformly distributed throughout sufficient to impart non-blocking characteristics to the film, said film being essentially free of odor and taste and rendering said paper resistant to staining and penetration by hot and cold beverages including water, coffee, tea, cocoa, milk and fruit juices brought into contact with the coated surface of the paper.

3. Paper surface-coated with a baked-on clear, transparent strongly-adherent continuous film from a water emulsion of resin solids consisting essentially of water emulsified polystyrene, water emulsified styrene-butadiene copolymer and water emulsified polyethylene, the styrene moieties of the polystyrene and the copolymer together being equal in weight to approximately four times the weight content of the butadiene moieties, and the poly-

ethylene comprising from about .625% to 3.32% by weight of the film, said film being essentially tack-free and providing resistance to penetration and staining by ordinary foods and beverages both hot and cold.

4. As a method of improving the resistance of paper to staining and penetration by ordinary foods and beverages, both hot and cold, the steps of coating a surface of the paper with a layer of an aqueous emulsion of polymeric material from the group consisting of (a) water emulsified styrene-butadiene copolymer and (b) water emulsified polystyrene mixed with water emulsified styrene-butadiene copolymer, said emulsion further containing an amount between about .625% and about 3.32% by weight of water emulsified polyethylene sufficient to introduce non-blocking characteristics to the fused film left on the surface after heating, the butadiene moieties of said polymeric material not exceeding approximately one-half thereof and the styrene moieties being not less than one-half thereof, heating the aqueous emulsion layer to drive out the water, thereafter raising the temperature of said layer to a temperature where the remaining solids will fuse into a continuous film, and then cooling to leave a clear transparent protective film strongly adherent to the paper.

5. As a method of improving the resistance of paper to staining and penetration by ordinary foods and beverages, both hot and cold, the steps of coating a surface of the paper with a layer of an aqueous emulsion of water emulsified polystyrene, water emulsified styrene-butadiene copolymer and water emulsified polyethylene, the polyethylene comprising from about .625% to 3.32% by weight of the solids in said emulsion, the butadiene moieties of said copolymer being equal to from about 15 to 25% by weight of said solids, and the styrene moieties of the copolymer and polystyrene together comprising the balance of the solids, heating the aqueous emulsion layer to drive out the water, thereafter raising the temperature of said layer to where the remaining solids will fuse into a continuous film, and then cooling to leave a thin clear transparent protective film strongly adherent to the paper.

6. A water emulsion coating composition free of organic solvent and consisting essentially of water emulsified resin solids, said emulsified resin solids constituting (I), as a major ingredient, polymeric material from the group consisting of (a) water emulsified styrene-butadiene copolymer and (b) a mixture of water emulsified styrene-butadiene copolymer and water emulsified polystyrene, and (II), as a modifier for the polymeric material, water emulsified polyethylene in an amount between about .625% and 3.32% by weight of the total resin solids, the butadiene moieties of said polymeric material comprising from about 15 to 25% by weight of the total resin solids, and the styrene moieties of said polymeric material comprising the balance, said composition being capable, when applied as a thin coating to paper and heated to the fusion temperature of the solids, of forming a thin continuous film that is strongly adherent to the paper, that is essentially tack-free and which provides the thus coated paper with marked resistance to penetration and staining by ordinary foods and beverages, both hot and cold.

7. A water emulsion coating composition free of organic solvent and consisting essentially of water emulsified resin solids diluted in water such that the total resin solids content of the composition comprise from 25 to 50% by weight of the composition, said emulsified resin solids constituting (I), as a major ingredient, polymeric material from the group consisting of (a) water emulsified styrene-butadiene copolymer and (b) a mixture of water emulsified styrene-butadiene copolymer and water emulsified polystyrene, and (II), as a modifier for the polymeric material, water emulsified polyethylene in an amount between about .625% and about 3.32% by weight

of the total resin solids, the butadiene moieties and said polymeric material comprising from about 15 to 25% by weight of said polymeric material and the styrene moieties comprising the balance of said polymeric material, said composition being capable, when applied as a thin coating to paper and heated, of fusing into a thin continuous film that is strongly adherent to the paper, that is essentially tack-free and which provides the thus coated paper with marked resistance to penetration and staining by ordinary foods and beverages, both hot and cold, the amount of polyethylene being sufficient to introduce non-blocking characteristics to said film.

8. A water emulsion coating composition free of organic solvent and consisting essentially of water emulsified resin solids, said emulsified resin solids constituting water-emulsified styrene-butadiene copolymer, water emulsified polystyrene and water-emulsified polyethylene, the polyethylene representing between .625% and 3.32% by weight of the total resin solids, the butadiene moieties of said copolymer representing from about 15 to 25% by weight of the total resin solids and the styrene moieties of the copolymer and the polystyrene together comprising the balance, said composition being capable, when applied as a thin coating to paper and heated, of fusing into a thin continuous film that is strongly adherent to the paper, that is essentially tack-free and which provides the thus coated paper with marked resistance to penetration and staining by ordinary foods and beverages, both hot and cold.

9. A water emulsified coating composition consisting essentially of from about 25 to 50% by weight of emulsified resin solids in water, said emulsified resin solids constituting water emulsified styrene-butadiene copolymer, water emulsified polystyrene and water emulsified polyethylene, the polyethylene representing between .625% and 3.32% by weight of the total resin solids and the styrene-butadiene copolymer and polystyrene representing the balance of said resin solids, the styrene and butadiene moieties of said polystyrene and copolymer together being in approximate weight ratios of 4 parts styrene to 1 part butadiene, said composition being capable, when applied as a thin coating to paper and heated, of fusing into a thin continuous film that is strongly adherent to the paper, that is essentially tack-free and which provides the thus coated paper with marked resistance to penetration and staining by ordinary foods and beverages, both hot and cold.

10. A water emulsion coating composition free of organic solvent and consisting essentially of water emulsified resin solids, said emulsified resin solids constituting water-emulsified styrene-butadiene copolymer, water emulsified polystyrene and water emulsified polyethylene, the polyethylene representing about 1.5% by weight of the total resin solids, the butadiene moieties of said copolymer representing from about 15 to 25% by weight of the total resin solids and the styrene moieties of the copolymer and the polystyrene together comprising the balance, said composition being capable, when applied as a thin coating to paper and heated, of fusing into a thin continuous film that is strongly adherent to the paper, that is essentially tack-free and which provides the thus coated paper with marked resistance to penetration and staining by ordinary foods and beverages, both hot and cold.

11. A container formed of paper and having its interior surface coated with a baked-on, clear transparent, continuous film deposited from a water emulsion of polymeric material from the group consisting of (a) styrene-butadiene copolymer and (b) mixture of polystyrene and styrene-butadiene copolymer, wherein the styrene moieties of said polymeric material comprise the major portion thereof and the butadiene moieties comprise the minor portion thereof, said film further containing 1 to 2% of polyethylene uniformly distributed through said polymeric

material, said film strongly adhering to the interior surface of the paper container but not deeply impregnating the paper, and said film imparting heat-insulating as well as non-blocking characteristics to the container and improved resistance to penetration, staining and disintegration of the paper when used to store hot and cold beverages such as coffee, tea, milk, cocoa and fruit juices, said film further being essentially free of taste and odor while tending to eliminate the taste of the paper over which it is coated.

12. Paper surface-coated with a continuous transparent, adherent heat-fused film from a water emulsion of resin solids consisting essentially of polymeric material from the group consisting of (a) water emulsified styrene-butadiene copolymer and (b) water emulsified polystyrene in admixture with water emulsified styrene-butadiene copolymer, the butadiene moieties of said polymeric material comprising from 15 to 25% by weight and the styrene moieties comprising the balance of said polymeric material, said solids further including approximately 1 to 2% by weight of water emulsified polyethylene uniformly distributed therethrough, said film being essentially free of odor and taste and rendering said paper resistant to staining and penetration by hot and cold beverages including water, coffee, tea, cocoa, milk and fruit juices brought into contact with the coated surface of the paper.

13. Paper surface-coated with a baked-on clear, transparent strongly-adherent continuous film from a water emulsion of resin solids consisting essentially of water emulsified polystyrene, water emulsified styrene-butadiene copolymer and water emulsified polyethylene, the styrene moieties of the polystyrene and the copolymer together being equal in weight to approximately four times the weight content of the butadiene moieties, and the polyethylene embodying 1 to 2% by weight of the film, said film being essentially tack-free and providing resistance to penetration and staining by ordinary foods and beverages both hot and cold.

14. As a method of improving the resistance of paper to staining and penetration by ordinary foods and beverages, both hot and cold, the steps of coating a surface of the paper with a layer of an aqueous emulsion of polymeric material from the group consisting of (a) water emulsified styrene-butadiene copolymer and (b) water-emulsified polystyrene mixed with water emulsified styrene-butadiene copolymer, said emulsion further containing from about 1 to 2% by weight of water emulsified polyethylene, the butadiene moieties of said polymeric material not exceeding approximately one-half thereof and the styrene moieties being not less than one-half thereof, heating the aqueous emulsion layer to drive out the water, thereafter raising the temperature of said layer to where the remaining solids will fuse into a continuous film, and then cooling to leave a clear transparent protective film strongly adherent to the paper.

15. As a method of improving the resistance of paper to staining and penetration by ordinary foods and beverages, both hot and cold, the steps of coating a surface of the paper with a layer of an aqueous emulsion of water emulsified polystyrene, water emulsified styrene-butadiene copolymer and water emulsified polyethylene, the polyethylene comprising from about 1 to 2% by weight of the solids in said emulsion, the butadiene moieties of said copolymer being equal to from about 15 to 25% by weight of said solids, and the styrene moieties of the copolymer and polystyrene together comprising the balance of the solids, heating the aqueous emulsion layer to drive out the water, thereafter raising the temperature of said layer to where the remaining solids will fuse into a continuous film, and then cooling to leave a thin clear transparent protective film strongly adherent to the paper.

16. A water emulsion coating composition free of organic solvent and consisting essentially of water emulsified resin solids, said emulsified resin solids constituting

(I), as a major ingredient, polymeric material from the group consisting of (a) water emulsified styrene-butadiene copolymer and (b) a mixture of water emulsified styrene-butadiene copolymer and water emulsified polystyrene, and (II), as a modifier for the polymeric material, water emulsified polyethylene in an amount equal to about 1 to 2% by weight of the total resin solids, the butadiene moieties of said polymeric material comprising from about 15 to 25% by weight of the total resin solids, and the styrene moieties of said polymeric material comprising the balance, said composition being capable, when applied as a thin coating to paper and heated to the fusion temperature of the solids, of forming a thin continuous film that is strongly adherent to the paper, that is essentially tack-free and which provides the thus coated paper with marked resistance to penetration and staining by ordinary foods and beverages, both hot and cold.

17. A water emulsion coating composition free of organic solvent and consisting essentially of water emulsified resin solids diluted in water such that the total resin solids content of the composition comprise from 25 to 50% by weight of the composition, said emulsified resin solids constituting (I), as a major ingredient, polymeric material from the group consisting of (a) water emulsified styrene-butadiene copolymer and (b) a mixture of water emulsified styrene-butadiene copolymer and water emulsified polystyrene, and (II), as a modifier for the polymeric material, water emulsified polyethylene in an amount equal to about 1 to 2% by weight of the total resin solids, the butadiene moieties of said polymeric material comprising from about 15 to 25% by weight of said polymeric material and the styrene moieties comprising the balance of said polymeric material, said composition being capable, when applied as a thin coating to paper and heated, of fusing into a thin continuous film that is strongly adherent to the paper, that is essentially tack-free and which provides the thus coated paper with marked resistance to penetration and staining by ordinary foods and beverages, both hot and cold.

18. A water emulsion coating composition free of

organic solvent and consisting essentially of water emulsified resin solids, said emulsified resin solids constituting water emulsified styrene-butadiene copolymer, water emulsified polystyrene and water emulsified polyethylene, the polyethylene representing about 1 to 2% by weight of the total resin solids, the butadiene moieties of said copolymer representing from about 15 to 25% by weight of the total resin solids and the styrene moieties of the copolymer and the polystyrene together comprising the balance, said composition being capable, when applied as a thin coating to paper and heated, of fusing into a thin continuous film that is strongly adherent to the paper, that is essentially tack-free and which provides the thus coated paper with marked resistance to penetration and staining by ordinary foods and beverages, both hot and cold.

19. A water emulsified coating composition consisting essentially of from about 25 to 50% by weight of emulsified resin solids in water, said emulsified resin solids constituting water emulsified styrene-butadiene copolymer, water emulsified polystyrene and water emulsified polyethylene, the polyethylene representing about 1 to 2% by weight of the total resin solids and the styrene-butadiene copolymer and polystyrene representing the balance of said resin solids, the styrene and butadiene moieties of said polystyrene and copolymer being in approximate weight ratios of 4 parts styrene to 1 part butadiene, said composition being capable, when applied as a thin coating to paper and heated, of fusing into a thin continuous film that is strongly adherent to the paper, that is essentially tack-free and which provides the thus coated paper with marked resistance to penetration and staining by ordinary foods and beverages, both hot and cold.

References Cited in the file of this patent

UNITED STATES PATENTS

2,616,864	Donaldson et al. _____	Nov. 4, 1952
2,726,967	Eger et al. _____	Dec. 13, 1955
2,805,962	Hendricks _____	Sept. 10, 1957
2,944,040	Pollock et al. _____	July 5, 1960