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GREASE REPELLANT PAPER

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This invention relates to grease-proof paper or one which is relatively resistant to penetration by greasy substances and to the process of making same, and the invention also includes as an article of manufacture containers made from such grease-resisting paper.

In using the term "paper" herein, I embrace not only the thinner grades of paper, but also the heavier grades, particularly those designated as board.

The present invention enables thin grease-resisting paper to be made, which in itself is not sufficiently thick or rigid to be self-supporting, but may be employed as a lining for containers made of stiffer material. On the other hand by treating paper board in the manner described herein, I am enabled to secure a sheet which has sufficient strength and rigidity as well as grease and water impenetrability to be employed as the sole stock in making boxes, cartons, ice cream containers, milk and other liquid containers, oyster pails, and the like.

It is a great advantage in making boxes not to be obliged to insert a special lining or inner wrapper of parchment paper, viscose sheet, and the like, and a desirable form of the present invention enables a grease-resisting container, such for example as a cracker, biscuit or caddy box, to be made without resort to a sheet of parchment or viscose as a lining material or inner wrapper.

The procedure set forth in the present invention is applicable to various grades of paper, such as wrapping paper (e. g., "butchers' wrap", "butter wrap", "candy wrap", and the like) but may be used to advantage with cheaper kinds of paper or board, particularly those containing ground wood. Thus I am able to employ a mixture of ground wood and sulphite pulp, and the like, to make a board suitable for the purpose. I do not, however, limit myself to any particular grade or thickness of paper and paper board.

The paper may be suitably sized if desired with rosin size or with wax emulsion, or with mixtures of rosin size and wax emulsion, or the paper, during formation may be built up of layers of pulp with intermediate layers of asphalt or other waterproofing emulsion, and the like. When asphalt board is used in a mill, great care must be taken to keep the scrap or trimmings of the cutting machines from getting into the waste which is returned to the beaters; as a few fragments of asphalt will ruin a large batch of paper. The resins concerned with the preferred form of the invention do not cause such defacement and may be used to best advantage in or on paper which does not carry any asphalt.

The invention also sets forth as one preferred feature the employment of such resins in an emulsified form, preferably dispersed in water.

By the employment of the latter vehicle any hazards which might result from the employment of volatile organic solvents are eliminated.

The grease-resistant resins and balsams of the synthetic type, comprise a group having different chemical and physical properties, but having in common the grease-repellant characteristic. The group includes resins made from crystalline organic acids and their anhydrides, e. g., phthalic, diphenic, succinic, citric, tartaric, benzoic, salicylic, malic, maleic, fumaric acids and the like, with such chemically different substances as glycols, chlorhydrins, glycol ethers, also glycerol, polyglycerol, pentaerythritol, and organic oxides such as ethylene and butylene oxides. In conjunction with such crystalline acids, and the like, I prefer also to employ another type of acid, namely; a fatty acid of an animal or vegetable oil, or what may be termed collectively the oil-acids (fat-acids).

Cottonseed phthalic glyceride resin, as set forth in my prior applications, may be employed to advantage herein. It is cheaply prepared from readily available materials. Similarly the fatty acids of other vegetable oils such as peanut oil, corn oil, soya bean oil, and the like, also those of castor oil, may be employed in preparing a resin appropriate for use in carrying out the present invention. In application, Serial No. 609,136, filed December 26, 1922 for Artificial resins from glycerol and the like, there is disclosed and claimed the production of phthalic glyceride types of resins, including modifying ingredients. In application, Serial No. 61,839, filed October 10, 1925 for Resinous products, their compositions and process of making same, there is described and claimed the production of resins and the resins themselves obtained from polyhydric alcohol, polybasic acids, and glyceride oils including both drying and semi-drying oils, and also the acids derived from such oils. In application, Serial No. 144,647, filed October 27, 1926, entitled "Resinous bodies and compositions and process of making same", there are described and claimed the resins and processes of making such resins including resins of the phthalic glyceride type containing a component derived from glyceride oils, and particularly distilled fatty acids obtained from such oils. The present invention is concerned with the utilization of such resins in the production of water emulsions, and in paper products carrying such resins or emulsified resins.

The following is an illustration of one manner of procedure in making a "grease-proof" paper with emulsions of synthetic resin:

200 parts by weight of boiling water containing 3 per cent of concentrated ammonium hydroxide solution was stirred and 60 parts of molten cottonseed phthalic glyceride resin was

slowly added thereto. The resin was heated to about 110° C. before introduction into the water vehicle. A good emulsion was obtained in this manner. When flowed on glass and allowed to dry a fairly transparent resinous film resulted. This emulsion was applied to a sheet of paper forming a thin layer which was dried yielding a grease-repellant surface. A laminated product was made by applying the emulsion to one surface of paper and applying a second sheet of paper thereon, pressing together and allowing to dry. In this way the grease-repellant medium exists as an intermediate layer and therefore does not necessarily alter the appearance of the exterior or exposed surfaces of the laminated product.

In like manner sheets of a greater number of plies were formed by cementing one sheet of paper to another with the resin dispersion to produce a thick paper board of good grease-repellant qualities, that is to say, the grease or oil would not penetrate from one side of the board to the other owing to the resistance to penetration offered by the interposed layer of the grease-repellant synthetic resin. Furthermore, such layer also exerts a moisture-resisting action and hence water does not readily penetrate. The invention therefore may concern a single sheet of paper or board rendered resistant in this manner on either one surface or on both, or two or more sheets of paper, that is, a plurality of sheets may be cemented together with intermediate layers of the synthetic resin. Such sheets may or may not have a coating of the resin on the exterior surface. This heavier grade of paper may be fabricated into containers of any suitable character such, for example, as those previously noted.

Various methods may be employed in the application of the resinous dispersion and its consistency may be varied from a thin to a heavy emulsion depending on the particular requirements in hand.

In a similar manner other phthalate resins or those made from malic, citric, tartaric, salicylic, benzoic, succinic, and other acids or anhydrides, preferably in combination with one of the oil acids may be used if desired. The fatty acids of coconut, corn, soya bean and tallow, thus are included. The cottonseed phthalic glyceride resin satisfies the requirement of cheapness of production, of ready emulsifiability, and of excellent grease-repellant and water-repellant qualities, and therefore constitutes my preferred resinous composition employed for the purposes hereof.

Other resins within the preferred zone are oleic phthalic glyceride, stearic phthalic glyceride and the corresponding palmitic or palmito-stearic phthalic glyceride and analogous glycol products. Other saturated fat acids such as mono or dihydroxy stearic acids may be used.

The stearic resins are of a harder type, while the oleic resins are more likely to be soft and somewhat sticky. The choice of the resin for a particular use will depend on the manner of use; e. g., a softer and more sticky resin may be used as a cement or adhesive to prepare ply board, while a harder resin is better adapted for exterior surfacing.

Some of the harder resins which may emulsify with difficulty may be softened by the addition of sufficient volatile solvent to render the mix quite liquid at the boiling point of water. Or emulsification may be carried out in an autoclave pro-

vided with a good agitator and the pressure on the mixture of alkaline water and the resin raised, by applying heat, to correspond to a temperature above the melting point of the resin.

While I prefer to apply the grease-impervious resin in emulsion or dispersion form, as set forth above, I may, in some cases, make the application by first heating the resin above its melting point and forming a coating of the molten resin on the sheet of paper, an excess being removed by roll or scraper. The paper should be well dried in this case before the molten resin is applied.

In Serial No. 214,781 I have disclosed the use of nitrocellulose in conjunction with the grease-arresting resin. Nitrocellulose, however, imposes restrictions on the character of the organic solvents which can be employed and by omitting the nitrocellulose cheaper solvents may be used. Although, according to the present invention, nitrocellulose is not used, I do not preclude the employment of wax in the resin solution as described in Serial No. 214,781 and in my copending patent applications on floor covering.

The coating or impregnating step may be carried out by means of any appropriate coating apparatus, as by passing through a set of coating rolls or through a bath and squeeze rolls. Spraying may be used in some cases.

Drying and calendering, cold or hot, may follow the above step.

A dye soluble in the resin may be used in some cases to give the coating a suitable tint; this being desirable when treating some grades of wrapping paper to make a substitute for so-called parchment paper. The paper, for example, a bleached sulphite, may be coated on one side only with the dyed resin and the tint thus produced serves to indicate which side of the paper is to come in contact with the meat, fish, butter or other moist and oily or greasy food products which are generally wrapped in parchment paper.

For economy, I prefer to use the minimum proportion of resin which will accomplish the purpose. Thus, on a good grade of white (sulphite) wrapping paper I may apply from 2 to 5 pounds of the resin per 1000 square feet of paper (one side only). With such a thin coating practically no change in the surface of the paper is visible, hence the introduction of a dye serves to make evident which side of the paper carries the otherwise invisible grease-arrester.

Still another method of applying the grease-arrester is to add it as an emulsion to the beater, precipitate the resin on the pulp fibre by adding alum or other coagulant and forming the pulp into a sheet in any suitable manner, hot calendering if and as required.

This method avoids the subsequent drying when an emulsion or solution of the resin is applied to the finished paper sheet or web. The trimmings, cuttings or punchings constituting waste or scrap in forming the paper or board into containers, and the like, may be returned to the beater.

The addition to the resin of other substances to modify, extend or dilute the grease-arresting resin is not precluded, provided the essential properties of the resin are not impaired to an extent inconsistent with the operation in hand.

For box or container board there may be applied to the surface which is to form the inner part thereof, a liner containing or carrying an

adequate proportion of the grease-arrester to prevent the fat from highly shortened biscuit or cookies from penetrating to the exterior of the container. The other side of the board (exterior of the box) may carry a liner which is made from paper sized with paraffin wax emulsion and is rendered thereby highly resistant to the transmission of water-vapor from the outer air into the contents of the package.

The board of the container therefore is provided with the inner liner (or coating) of the grease-arrester and the outer liner containing moisture-repellant wax.

Methods of making paper containing such wax do not form any part of the present invention.

In treating paper heavily sized with rosin by the solvent impregnation procedure, there is danger that the solvent such as benzol will dissolve the rosin size and that the latter mingling with the grease-repellant resin will lower the grease-arresting property. Paper of this character may be treated with the grease-repellant resin emulsified in an aqueous medium to avoid solution of the sizing present.

Without committing myself to a particular formula for making the grease arresting resin, the following will serve in an illustrative way.

	Parts
Glycerol	100
Phthalic anhydride	160
Distilled fatty acids of cottonseed oil	90
(The proportions are by weight.)	

A batch in these proportions is heated in an aluminum kettle to 230-250° C. to yield a resin of melting point 62-64° C. (ball and ring method) and of acid number 20-24. It is soluble in benzol or toluol or in a mixture of benzenoid hydrocarbons and acetone, alcohol, and the like. It is light colored and has the property of ease of emulsification with slightly alkaline water to make a very smooth finely-divided composition, leaving, on drying in thin layers, a substantially transparent colorless coating of a much more uniform character than would be expected to form from the drying of a resin dispersion. This quality is of assistance in the production of impervious films or coatings.

The hardness and other properties of the resin may be varied by changing the proportions in the foregoing formula.

In general, however, proportions should be used which yield a resin of low acid number, if the coating composition is to be used in making wrapping paper or board intended to contain food products. A low acid number indicates an adequate completion of the reaction to avoid contamination of the food by phthalic, succinic or other acid employed in making the resin.

Paper employed in contact with wet and greasy foods may carry a coating of rosin cottonseed phthalic glyceride resin or a corresponding resin in which congo or other copal replaces the rosin in whole or in part. A small proportion of an acid natural resin chemically combined in the synthetic resin may be used to furnish a higher water test product.

In Serial No. 609,136 filed December 26, 1922, I have referred, among others, to resins such as oleic phthalic glyceride and stearic phthalic glyceride as well as to phthalic glyceride, tartaric glyceride, also resins derived from lactic and from mucic acids and have called attention to the employment of such products with paper and other fibrous material. Thus, phthalic

glyceride resin is dissolved in hot benzol or in a mixture of alcohol and benzol and paper is impregnated therewith or the resin is incorporated in any other suitable manner. The present application continues and elaborates the disclosure of Serial No. 609,136.

The paper or board of the present application carrying the synthetic resin may, if desired, be hot pressed to form a shaped or fashioned article such as a box or other container, hood cap, and the like.

A stearic phthalic glyceride resin may be made from:

	Parts by weight
Stearic acid	60
Phthalic anhydride	160
Glycerol	100

These components are heated together at 240° C. for 1 hour. In one case a resin of acid number about 22 and melting point approximately 60° C. was obtained.

A stearic toluyl-benzoic glyceride resin may likewise be used in emulsion form (dispersed in water containing a few percent of ammonium hydroxide).

Benzoic phthalic glyceride is somewhat more difficult to emulsify with aqueous ammonium hydroxide. The latter is desirable as an emulsifying alkali instead of the fixed alkalies as the ammonia evaporates on exposure and therefore the fibre in contact with the grease-arrester is quickly freed from alkaline substances. This elimination is rendered more expeditious by heating, as by drying on hot rolls or in a drying room or heated festooning chamber.

An aqueous medium containing 3% each of ammonium hydroxide and gum arabic yields a better emulsion. Dispersions made with the aid of gum tragacanth, Irish moss and the like also may be employed. Likewise hydrophylic clays such as bentonite may be used to assist in securing the required degree of dispersion.

The colloid mill may be used in preparing the foregoing dispersions, either of the proper strength to be applied directly to the paper or as a concentrate which is to be diluted with water before application to the surface of the paper, or prior to introduction into the heater.

A complex resin containing both combined stearic and benzoic acids is made as follows:

	Parts by weight
Stearic acid	5
Benzoic acid	3
Phthalic anhydride	16
Glycerol	10

The temperature is carried to 250° C. and is held at this point for 1 hour.

A resin obtained in this way exhibited a melting point of 66° C. and an acid number of 42.

Still another resin obtainable from readily available raw materials is the following:

	Parts by weight
Animal tallow fatty acids	9
Phthalic anhydride	16
Glycerol	10

Heated to 245-250° C. and held at about this temperature for 1 hour, yielded a resin of acid number 36.5 and melting point (ball and ring method) of 62° C.

A resin made from phthalic anhydride and glycerol alone, using a few per cent of acetamide as a catalyst, was emulsified and applied hot to

paper. The latter was hot calendered after drying. A coating on the surface acted as a grease-arrester. Two sheets of paper cemented together by a coating of this dispersion, as an intermediate layer only, absorbed grease in the outer unprotected part of each sheet, but the grease did not penetrate through from one sheet to the other as the interposed grease-arrester effectually checked the diffusion in this direction. The grease spread slowly laterally only. Such a lateral spread is checked by giving the outer surfaces of the sheets an appropriate coating of the grease-arrester.

The phthalic glyceride resin is more difficult to emulsify than the resins made with the aid of the higher fatty acids and I prefer to employ the latter. Despite the presence in combined form in the resin of such higher fatty acid the coating appears to be more resistant to fat penetration than is the case with the more simple phthalic glyceride resin itself. Neither is the benzoic phthalic glyceride resin quite so effective as a grease-arrester as the higher fatty acid resins, possibly because the emulsion used was not in as perfect dispersion.

An advantage in using emulsions instead of solutions of the resin, in addition to those already pointed out, is that the resin in emulsified form deposits more nearly at the surface of the paper while the solution penetrates and impregnates. By surfacing the paper with an emulsion, less resin is required than is demanded when the resin is employed in solution in an organic solvent vehicle. The emulsion therefore coats rather than impregnates.

Resins of a somewhat different character also may be made by heating castor oil, phthalic anhydride and glycerol together. A resin of this modified type may be emulsified in hot dilute aqueous ammonium hydroxide solution and the dispersion applied to paper.

Castor phthalic glyceride resin, 60 parts by weight, was heated to 110° C., and was poured slowly with strong agitation into 200 parts boiling water containing 6 parts concentrated ammonium hydroxide solution.

This dispersion was applied to several types of paper, e. g., (a) heavy kraft paper of a thickness 0.18 m.m., (b) a ground wood and sulphite pulp board, thickness 0.6 m.m., (c) a somewhat similar board of thickness 0.5 m.m. which was initially quite water-resistant due to the addition of paraffin wax emulsion to the beater when the pulp for this board was being prepared.

Board (b) was coated on one side with this emulsion and dried. A sheet of similar board was pressed against the coated surface and the two sheets hot-calendered together. This gave a laminated sheet. Some of the latter was placed between dies and spoons were punched therefrom. In another case spoons were pressed from a triplex paper made by dipping one sheet of paper into the emulsion bath to coat both sides, drying and hot-pressing a sheet on each side of this coated sheet to form the triplex laminated product.

The foregoing examples specify particularly glyceride resins made from raw materials readily available or easily produced as the demand requires. This is a matter of importance to the paper manufacturer who is thus able to utilize the process of the present invention, with the assurance that mill operation will not be hindered by lack of supply of the resin raw materials.

Therefore the disclosure of the present invention is one which is made with the foregoing in view and should not be construed as a limitation precluding the use of other resins dissimilar chemically, but having similar or analogous grease-arresting properties.

Other acids than the carboxylic acids such as various sulphonic acids, nitro acids, acid chlorides, and the like, may be used in making the grease-arresting product.

Among the various synthetic resins which may be incorporated with the foregoing in some cases are the vinyl resins such as vinyl chloride or vinyl acetate in polymerized form, methylene ketone resins, urea formaldehyde products and so forth. The urea-formaldehyde resins usually contain loosely combined formaldehyde which may be evolved after the paper is put to use. Care should be taken in this case to heat-treat or chemically-treat the resin or the coating therefrom to overcome the slow evolution of formaldehyde from papers intended for wrapping food products.

It should be understood that I do not limit myself to any particular thickness of the resinous surfacing, coating or impregnation, but may apply in such dilution that the coating is invisible or practically so, or may increase the concentration to provide a coating or impregnation of considerable substance. Thus a coating may be produced from a fairly concentrated dispersion which is glossy and affords a desirable lustrous finish to the paper.

For example, using the tallow phthalic glyceride resin described above, I have prepared an emulsion by heating in water rendered slightly alkaline with potassium hydroxide and have found, when the resulting milky fluid or emulsion is applied freely to sized paper that a transparent glossy surface results on drying.

Thus I am able to use the fatty acids of shortening fats such as cottonseed, corn, soya, coconut, tallow, lard, and the like, in making a grease-resisting resin for wrapping paper, cartons, and so forth, employed in handling foods. The same kind of fat may be used in making the grease-arrester as is used in preparing the food which is to be placed in contact paper carrying the grease-arrester. Thus, wrapping paper to be used in packaging lard may carry a surfacing of a grease-arresting ester resin of the lard phthalic glyceride type, preferably present in non-visible proportion. Such wrapping paper may carry the invisible coating of a synthetic resin grease-arrester of the glyceride type applied in an emulsified condition; for which purpose the fat-acid phthalic glyceride resins are highly desirable owing to their ease of emulsification with dilute alkali. A more complex form of paper product is one, the pulp used in which has been sized in the beater with wax emulsion (with or without rosin size), that carries a coating (visible or non-visible) or impregnation of a grease-repellant synthetic resin.

Further it should be pointed out that a major use for the grease-arresting paper is in the conveyance or packaging of foodstuffs and that any substance in the grease-arrester which may contaminate foods should be avoided. Resins evolving powerful and offensive odors such as naphthalene, nitrobenzene or those containing in loose combination some of the lower aliphatic monobasic carboxylic acids (from say 4 to 8 carbon atoms) are ill-suited for the foregoing purpose. Acids of a fixed character yielding stable

resins such as the fat or oil-acids are desirable for use in making the ester resin and have the additional advantage of being closely related to the fats (shortening or other fatty or oily substance) commonly found in natural and prepared foods. One should, for example, avoid the employment of a resin which, in paper used for wrapping butter, gives off butyric exhalations or other offensive odors of volatile lower fatty acids suggestive of foul and rancid butter or other deteriorated foodstuffs.

Still another consideration of import when the resin is applied as an outer surfacing rather than as an inner or "ply" layer and especially when such surfacing is fairly heavy, is that of sticking of separate sheets that have been laid in a pile.

Harder resins than some of those specifically described may be required to make a non-adherent sheet and allow packs of sheets to be handled and shipped without loss by unintended sticking together.

The several resins containing in combination a fat-acid of an unsaturated type including the fat-acids from the drying and semi-drying oils, may be treated with one to several per cent of a hardening agent such as sulphur chloride and the resin thus modified applied in solution or suspension to the paper. If the resin is to be used in solution in organic solvents the proportion of sulphur chloride (mono or di chloride) should be low to preserve solubility. When the resin is to be applied as an emulsion the proportion of this hardening agent may be greater. An ammoniacal dispersion of the resin in water suffices to neutralize acidity arising from the sulphur chloride.

Other hardening agents are antimony trichloride, the phosphorus chloride and oxychlorides and other analogous halide-containing reagents.

Likewise a harder resin may be secured by reducing the proportion of fat-acid in resins containing this component.

Nitrocellulose as indicated in Serial No. 214, 781 acts as a co-operative hardening agent.

Thus a transparent paper was made by passing glassine paper through solutions of the resin, with and without treatment with sulphur monochloride (1 per cent) and with and without nitrocellulose. Untreated cottonseed phthalic glyceride showed the greatest tendency to "print", the same resin treated with the sulphur chloride provided a diminished tendency in this respect which disappeared completely when 25 per cent of the weight of the resin of nitrocellulose was incorporated in the solution.

Transparent paper resembling the viscose wrapping known as "cellophane" was thus readily obtained.

Another simple method of hardening many of these resins to a point past the "printing" stage is to "de-tack" by baking. The resin is, for example, heated in thin layers in an oven at a mild heat for several hours or until the melting point is raised a few degrees and tackiness is eliminated. For use with volatile organic solvents the baking should not be carried beyond the point of adequate solubility. If the baked resin is to be employed in aqueous dispersion, the baking may be advanced in some cases beyond the point of ready solubility while arresting the hardening before the resin becomes resistant to emulsification.

Paper coated with a hardened emulsifiable synthetic resin of a grease-arresting character con-

stitutes one form of the present invention. The invention also comprises paper substantially transparent, carrying a grease-arresting synthetic resin of a non-tacky nature. The resin thus may serve several purposes, e. g.

1. A grease-arrester.
2. A transparentizer.
3. A strengthener or binder.
4. A gloss or lustre producer.
5. A waterproofing agent or medium to reduce the transmissivity of water vapor (wrapping for cigarette packages, and so forth).

What I claim is:—

1. A covering suitable for greasy articles, consisting of a paper coated or impregnated with a polybasic organic acid-polyhydric alcohol resin containing a higher fatty acid in chemical combination, the resin being of a character and present in an amount sufficient to give substantial grease repellant properties to the paper.

2. A covering suitable for greasy articles, consisting of a paper coated or impregnated with polyhydric alcohol-polybasic organic acid resin containing cottonseed fatty acids in chemical combination, the resin being of a character and present in an amount sufficient to give substantial grease repellant properties to the paper.

3. A covering suitable for grease containing articles, consisting of paper coated or impregnated with a polybasic organic acid-polyhydric alcohol resin containing cottonseed oil fatty acids in chemical combination, the coating composition being subjected to hot calendering subsequent to its application to the paper and being of a character and present in an amount sufficient to give substantial grease repellant properties to the paper.

4. Paper sized with wax and carrying a coating of polybasic organic acid-polyhydric alcohol resin of a character and in an amount sufficient to give substantial grease resistance to the paper.

5. The process which comprises applying to paper an aqueous emulsion containing a polyhydric alcohol-organic carboxylic acid resin of a character and in an amount sufficient to give substantial grease repellant properties to the paper, and subsequently hot calendering the paper.

6. Paper coated or impregnated with polyhydric alcohol-polycarboxylic acid resin of a character and in an amount sufficient to impart substantial grease resistance thereto.

7. Paper coated or impregnated with a phthalic glyceride resin of a character and in an amount sufficient to impart substantial grease resistance to the paper.

8. Paper coated or impregnated with fatty acid modified phthalic glyceride resin of a character and in an amount sufficient to impart substantial grease resistance thereto.

9. A process of treating a body which comprises applying to a surface of such body, a water solution of a water-soluble salt of a polybasic acid-polyhydric alcohol resin.

10. A process of treating a body which comprises applying to a surface of such body, a water solution of a water-soluble salt of a polybasic acid-polyhydric alcohol resin, and rendering the resinous material water-insoluble.

11. A process of treating porous materials which comprises applying to such materials, a water solution of a water-soluble salt of a polybasic acid-polyhydric alcohol resin.

12. A process of treating porous materials which comprises applying to such materials, a water solution of a water soluble salt of a poly-

basic acid-polyhydric alcohol resin, and rendering the resinous material water-insoluble.

13. A process of treating porous materials which comprises applying to such materials, a water solution of a water soluble salt of a polybasic acid-polyhydric alcohol resin, and rendering the resinous material water-insoluble by treatment with an acid material.

14. A process of treating porous materials which comprises applying to such materials, a water solution of a water soluble salt of a polybasic acid-polyhydric alcohol resin, and rendering the resinous material water-insoluble by treating with a solution of a polyvalent metal salt to precipitate a polyvalent metal salt of the resin.

15. A process of improving the water and grease resistance of paper which comprises coating the paper with a water solution of a water soluble salt of a resin of the polybasic acid-polyhydric alcohol type, and rendering the resin water-insoluble.

16. A process of improving the water and grease resistance of paper which comprises coating the paper with a water solution of a water-soluble salt of a resin of the polybasic acid-polyhydric alcohol type and rendering the resin water-insoluble by treatment with an acid material.

17. A process of preparing transparent paper which comprises treating thin paper with a water solution of a water-soluble salt of a resin of the polyhydric alcohol-polybasic acid type and rendering the resin water-insoluble.

18. A process of preparing transparent paper which comprises treating thin paper with a water

solution of a water-soluble salt of a resin of the polyhydric alcohol-polybasic acid type and rendering the resin water-insoluble by treatment with an acid material.

19. A process of treating porous materials which comprises applying to such materials, a water solution of an ammonium salt of a polybasic acid-polyhydric alcohol resin.

20. A coating composition comprising a polyhydric alcohol-polybasic acid resin emulsified in an aqueous medium with a small amount of an alkaline emulsifying agent.

21. A coating composition comprising a glycerol-phthalate resin emulsified in an aqueous medium with a small amount of an alkaline emulsifying agent.

22. As a composition of matter a synthetic resin containing in chemical combination the radicals of a polyhydric alcohol, a polybasic acid and a monobasic carboxylic acid containing several unsaturated linkages, said resin being emulsified in an aqueous medium with a small amount of an alkaline emulsifying agent.

23. A coating composition comprising a chemical reaction product of glycerol with phthalic acid and glyceride oil fatty acid, emulsified in an aqueous medium with a small amount of an alkaline emulsifying agent.

24. As a composition of matter a synthetic resin containing in chemical combination the radicals of a polyhydric alcohol, a polybasic carboxylic acid and a monobasic fatty acid, said resin being emulsified in an aqueous medium with a small amount of ammonia as an emulsifying agent.

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