

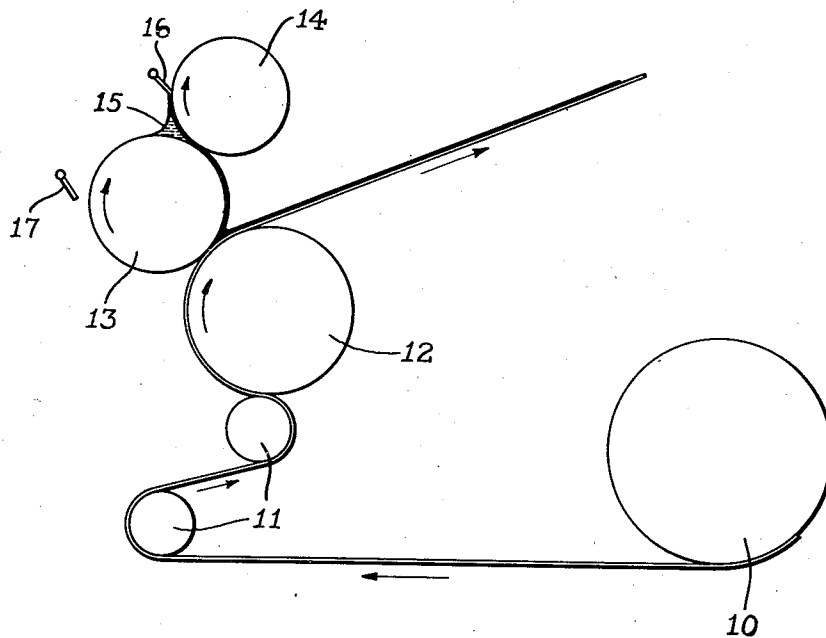
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WATERPROOF AND GREASEPROOF PAPER

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Inventors

Harry C. Fisher
James F. Thompson and
Walter E. Searcy

By *Marichal & Roe*
Attorneys

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WATERPROOF AND GREASEPROOF PAPER

Harry C. Fisher and James F. Thompson, Cincinnati, and Walter E. Sooy, Middletown, Ohio, assignors to The Gardner-Richardson Company, Middletown, Ohio, a corporation of Ohio

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9 Claims. (Cl. 91-68)

This invention relates to coating materials and processes and more particularly to the coating of paper products to provide proofing characteristics therein.

The principal object of the invention is to provide an inexpensive and easily applied coating material having characteristics of grease and oil resistance and flexibility such as to maintain the impervious character of the coating during the customary bending and forming operations and during the disruptive effects encountered during use.

It is a further object to provide a highly effective coated sheet of paper having an inexpensive grease and oil proof coating composition applied thereto and adapted to withstand the necessary bending and the like encountered during use.

It is a further object to provide a sheet of paper having a composite coating thereon including an overlying coating of high greaseproofness and a lower layer having characteristics of resistance to passage of moisture, oil, and grease and of flexible character such as to maintain the impervious character of the overlying coating in use.

It is a further object to provide such a sheet of paper which is highly resistant to the disintegrating effects of light such that the impervious character of the surfacing will not be readily deteriorated upon exposure to sunlight.

It is a further object to provide a simple and effective method for forming desired thin impervious films of coating upon the paper web and for forming composite coatings with the overlying coating bonded to the lower coating.

Other objects and advantages will be apparent from the description and the accompanying claims.

This application is a division of copending application Serial No. 167,758, filed October 7, 1937, now Patent No. 2,205,557, issued June 25, 1940.

The present invention relates to the provision of coatings upon paper or paper material especially where such paper material is adapted to be used in the production of containers or the like. The coating may be of different characteristics in accordance with the properties desired for various purposes, the coating being selected to embody and provide the desired resistance to penetration of moisture, grease, oil, and the like, and to provide varying degrees of flexibility. The coating may be applied to the formed container, or preferably it is applied to the paper material in sheet form and the coated sheet of paper then wound or formed into the desired form for the container with the coated surface of the sheet

forming the proofing surface to be effective in and upon the interior of the container. Where the coating composition is applied in this manner, it is important that the coating film have and retain such flexibility characteristics as to avoid rupture of the coated film upon the operations of bending and the like which are incident to the formation of the sheet into container form. In accordance with the present invention coating compositions are provided having such desired characteristics of resistance to penetration, and also having the proper flexibility to maintain an impervious coating film during the customary forming operations, and during such bending and the like as normally occurs in use. It is further found that such coating compositions are not subject to rapid deterioration under the action of light, as is the case in many instances where a rubber latex containing material is utilized. The coating composition made in accordance with the present invention, however, is remarkably resistant to deterioration even upon exposure to sunlight, such as may take place following the opening of the sealed container.

While the coating composition may be applied in a single coating surfacing or layer, it is usually preferred to form a multiple or composite coating in which a plurality of surfacings are applied one over the other. In this way a completely impervious surfacing is secured having the characteristics as desired and which is capable of retaining its imperviousness during use. The present invention provides coatings adaptable for this purpose, where more than a single coating layer is applied.

In accordance with the preferred practicing of the invention, a lower or base coating layer is applied to the sheet and an overlying coating thereafter applied of predetermined related characteristics with the base coating, such that the composite coating provides the desired properties of adequate resistance to penetration of grease and the like, and also the proper flexibility characteristics as described above, the coatings being intimately bonded to each other so that one does not strip from the other.

A coating composition suitable for forming a lower or base coating layer of this invention is made comprising a suitable glue which is modified to have improved characteristics of flexibility. The ordinary type of glue coating when dry is found to be relatively brittle, and not subject to such bending as necessary in order to provide for properly maintaining the impervious film upon bending of the paper to which it is applied. Ac-

cordingly the glue is combined with a suitable material having the effect of a plasticizer, the mixture being made down with water to a proper consistency for ready application, thereby providing a composition which will embody the proper degree of resistance to penetration of moisture, grease and the like and at the same time be adequately flexible in its formed and dried condition.

As examples of suitable compositions, the composition may comprise an animal glue melted down in water, together with a plasticizer chosen from the group comprising glycerine, and other polyhydric alcohols such as the hexahydric alcohol sorbitol, and also various glycols, invert sugars such as those named "Krist-O-Kleer," "Nulomoline," sulfonated oil such as sulfonated castor oil, and the like.

In a preferred composition approximately 100 parts of dry animal glue, 250 parts of water, and 150 parts of glycerine plasticizer are used. The plasticizer is utilized in the amount required for the purpose desired, up to the maximum amount which is compatible with the adhesive. The example given above contains approximately the maximum quantity of glycerine it is desired to use for commercial purposes. Where sorbitol is employed as the plasticizer up to about 230 parts thereof may be used. Smaller amounts of plasticizer may be satisfactorily employed where a lesser plasticizing effect is desired.

In the preparation of such composition the animal glue is soaked in water and heated to melt down the glue and the liquid plasticizer is dissolved in the heated mixture. As thus prepared the material may be used at once or cooled to room temperature and kept for later use. At room temperature such composition is a brown livery mass which easily liquefies when heated, heating preferably being performed indirectly as with closed steam pipes or a double jacketed kettle to prevent burning the glue. Where the composition must be stored for any appreciable time under warm conditions, a suitable preservative may be added thereto to prevent it from spoiling.

The composition may be coated onto the paper or paper material in a molten condition by any convenient means such as nip rolls, spreader bar, roller coater, doctor blades, or the like. It is usually found however that it is desirable to work the composition into the surface of the paper and to smooth the applied coating film by means of oscillating brushes, smoothing rolls, or the like. The quantity of the applied coating is regulated in accordance with the characteristics of the product desired, in the well known manner by control of the quantity of material applied to the sheet.

It is also found in accordance with this invention that improved results are obtained with a coating such as the above, particularly as regards improving the water-proofness of the coating, where the coating film is treated to "harden" the surface thereof. This step can be conveniently performed by treating the applied film with a so-called "hardening" material containing an aldehyde such as formaldehyde or other suitable material capable of coagulating and waterproofing the glue. A preferred manner of effecting such treatment is to spray a solution of formaldehyde in water, for example, a 40% formaldehyde solution, directly onto the wet glue treated surface, following which the treated sheet if in a continuous web passes through a

drier tunnel heated to a suitable temperature, for example, 170° F. to about 200° F., or over drum or other heated driers where the plasticized glue coating dries out and the hardening and waterproofing action of the formaldehyde is made effective. Where such formaldehyde-treated sheet immediately passes into a drying tunnel, an atmosphere of formaldehyde vapors develops therein which aids in bringing about the proper waterproofing or so-called "hardening" action.

Instead of treating the applied film of composition with the hardening agent, such agent may be incorporated into the glue solution, care being taken to avoid hardening of the glue prior to its application to the paper. Formaldehyde from trioxymethylene can be employed by dissolving the latter in the watery glue solution whereupon the heat from the dryer, preferably intensified, liberates the formaldehyde during the drying of the applied glue film. Alternatively, in place of using a formaldehyde material, potassium dichromate may be introduced into the solution and its hardening effect upon the glue developed by the subsequent exposure of the coated surface of the sheet to a source of daylight or of light rays suitable for this purpose.

The product produced in accordance with the foregoing procedure is a paper sheet coated on one or both sides as desired with a layer of plasticized, water and grease resistant, flexible glue, the tackiness, flexibility and thickness of which can be predetermined as desired in each individual case. Whereas the tendency of unplasticized, unhardened glue coating is to crack and flake upon exposure to atmospheric conditions, and to become dry or moist with corresponding changes in the atmospheric condition, the coated film formed in accordance with the present invention resists such atmospheric influence to a high degree, maintaining a substantially uniform and impervious film having sufficient flexibility to permit of bending the sheet in the usual forming operations, without rupture or destruction of the impervious coating film.

Instead of using animal glue as the base of the composition above described, other adhesive materials of similar physical characteristics and having properties of insolubility in oil can be used, for example, dextrine, casein, starch, soy bean flour and the protein derived therefrom, and the like.

In using casein it is soaked in water until properly softened, and then sufficient water and ammonia are added to insure properly dissolving the casein to make a thick solution containing about 14% casein by weight. An illustrative coating composition including casein comprises approximately 80% by weight of the casein solution and 20% of a plasticizer such as sorbitol, glycerin, or the like. Such coating composition is applied to the paper in the manner described above, treated with a hardening agent to increase its waterproofness, and dried to provide the finished coated sheet having the characteristics described.

Similarly dextrine may be made into a thick solution in water with the addition of some borax, the thick solution being mixed with a plasticizer as above described, the coating composition being applied to a paper sheet to form an impervious flexible coating film. A composition of this character however is not adapted to be hardened by the application of formaldehyde as is the case with the compositions above described.

Starch in its various forms from the variety known as "Pearl" to the treated starches which are known as "soluble" is likewise made into a thick solution in water, for example, 90 parts of water to 10 parts of starch, and 80 parts of this starch solution then mixed with about 20 parts of the plasticizer to form the coating composition, which can be applied as above described. This coating also is not susceptible to ready hardening by the application of formaldehyde.

In copending application Serial No. 76,607 filed April 27, 1936, and in the continuation application Serial No. 256,996, filed February 17, 1939, in the names of Fisher and Thompson, and assigned to the same assignee as this application, there is disclosed for use primarily as an adhesive a composition comprising a mixture of a water soluble glue, preferably having a plasticizer admixed therewith, with a tacky solution of a resinous material in an organic solvent. As an example of such composition, an animal glue, vegetable glue casein or dextrine is dissolved in water, preferably in the presence of a plasticizing material such as glycerine, ethylene glycol, invert sugars, sorbitol or sulphonated oils. The resinous material comprises phenol-formaldehyde, urea-formaldehyde, vinyl or glyptal resins, or a chlorinated rubber product, dissolved in organic solvents such as toluol. This mixture is passed through a homogenizer or emulsifier to secure a highly dispersed condition, and provides a product which at room temperature is a thick and toughly gelatinous mass. Very satisfactory results have been secured in accordance with the present invention through the application of such materials, applied in a heated and molten condition, as a base coating for application to a sheet of paper. By the addition of greater quantities of water, lower coating temperatures may be employed, application being entirely practicable at room temperature where sufficient water is utilized. A variation of the quantity of water, with resulting variation in the viscosity of the composition provides for preparation of coating compositions suitable for various conditions of application. Thus for example the character of the coating mechanism, and the ability of such mechanism to provide for the laying down of a uniform smooth surface film are important in connection with the characteristics of the composition as supplied to the machine. Such composition may however vary from approximately one part by weight of adhesive to nine parts of water, forming a thin composition, to three parts of adhesive to nine parts of water, or even higher, resulting in a relatively thick or viscous composition. Before or during the drying of this coating, the hardening action of formaldehyde or equivalent materials as above described may be utilized.

Another form of emulsion for purposes of forming a lower or base coating comprises one of the synthetic alkyl resinous group derived from a polybasic acid, a synthetic product of terpene origin, commonly designated by the trade name "Petrex." Such resins vary from hard to soft, from non-tacky to viscous, from water white to dark amber in color, and likewise vary considerably with respect to their solubility in oily materials.

When dissolved in an organic solvent such as toluol, for example in a 50% solution, the toluol may be emulsified completely into a water sol-

uble solution of plasticized casein. A typical formula is as follows:

125 pounds casein
200 gallons water
4 gallons concentrated ammonia in water
82½ gallons Petrex resin solution (equal weights of resin and toluol)
3 gallons formaldehyde 40%
5 gallons plasticizer, such as glycerin, made up to
400 gallons with water.

In making this emulsion, the casein is softened in water and dissolved with the aid of ammonia, the glycerine added, the formaldehyde carefully added in controlled amounts to prevent premature hardening of the casein, and finally the resin solution is added and thoroughly mixed in. This mixture then preferably is passed through an emulsifier to bring about the desired dispersion. The resin emulsion is coated onto the paper by suitable means, and dried to provide a lower base coating having highly effective grease, water and moisture-proofness, and likewise sufficient flexibility to serve as a flexible undercoating for the reception of an overlying coating.

If it is desired to color the coating, this may be accomplished by the use of organic dyes such for example as the dye Fuchsine, which gives a purplish-red shade. The coating may also be loaded with finely divided mineral material such as finely divided chromic oxide which gives a green shade and also acts as a mineral filler. As an example of finely divided white mineral filler the customary coating clays or one of the numerous titanium dioxide pigments may be successfully used. The addition of certain colored pigments such as some shades of green and black is also found to be of value in providing additional resistance to degradation of the impervious character of the film under the action of light.

Coating films made in accordance with the foregoing, with the exception of the starch and dextrine coatings, are found to have desirable characteristics of water, grease and oil proofness, and such coating may be applied in one or more layers to provide the desired degree of proofness for various purposes. However in the preferred practicing of the invention such coating composition forms a lower or base coating, adapted to receive an upper or overlying coating having additional resistance to penetration of grease and the like. For example such overlying coating may comprise a cellulose ester film, such as a film of nitrocellulose or cellulose acetate, or other cellulose compounds. Also such overlying coating may comprise a resinous material such as phenol and urea formaldehyde resins, glyptal resins prepared from a polyhydric alcohol and phthalic anhydride, vinyl resins such as Gelva, Petrex or alkyl resins, chlorinated rubber such as Torne-sit, and waxy materials, gums, etc. and various combinations thereof. These organic materials may be applied as a solution in suitable organic solvents, including the addition of resins and plasticizers as desired in order to secure characteristics of covering power, viscosity, flexibility, and the like. Further such coatings may be applied in emulsion form, very satisfactory results having been secured through utilization of an aqueous emulsion of cellulose ester such as nitrocellulose, or resin.

Since the plasticized hardened base coating tends to resist wetting it is desirable to formulate

the solvents or liquids of the overlying coating composition so that the proper degree of wetting such as to insure uniform coverage and adhesion, will be obtained. For example where solutions of cellulose ester such as nitrocellulose are used it is advantageous to use a high percentage of alcohol in the vehicle for this purpose, and omit or reduce the quantity of hydrocarbon liquids such as benzol, toluol and xylol.

It is also important that the upper coating composition be applied in such manner as to form a thin, completely impervious, adherent coating film. Where an ordinary pair of nip rolls are used to apply a solution of nitrocellulose, for example, over a glue-type base coat as contrasted with a lower coating composition including a rubber material, it has been observed that there is a tendency for the coating to be applied in a spotty or irregular manner over the surface of the lower coating. Apparently this occurs because of lack of "affinity" between the nitrocellulose solution and the base coating. Whereas the organic solvents of a cellulose solution exert a minute though effective solvent action on a rubber type base coating and thus tend to key into it, a similar solubility action apparently does not occur with the glue type of base coat. In order to overcome such condition, it has been found that if a uniform film of the coating is applied first to a coating roll, in the required depth and with uniformity, this film may then be transferred to the web with the formation of a completely uniform and impervious coating film which is firmly secured to and keyed into the base coating by solvent wetting action. As an example of a suitable apparatus for this purpose, attention is directed to the accompanying drawing showing a preferred embodiment thereof in which the roll of paper to be coated is shown at 10, being fed over guide rolls 11, to a contact roll 12. A roll 13 runs in contact with the surface of the sheet of paper as it passes over roll 12, and is driven in a direction opposite to the travel of the paper web. Adjustable means are provided to vary the contact between these two rolls. A smaller roll 14 runs in predetermined spaced relation with roll 13, and rotates in a direction opposite thereto. The coating liquid is supplied to the pool 15 formed between the nip of rolls 13 and 14. A doctor 16 serves to prevent the liquid from being carried around the surface of roll 14, thereby maintaining a substantially clean surface on roll 14 as it comes around to the nip. A removable doctor 17 may also be provided for use with roll 13 when paper is not being coated. Roll 14 preferably operates at a somewhat slower speed than roll 13, and has an adjustable spacing with respect thereto to provide for variation in the depth of the layer of coating film applied.

The operation of this apparatus is as follows: The coating material applied to pool 15 is carried into the nip of rolls 13 and 14, the upper roll 14 providing for the application of a smooth, homogeneous film of uniform thickness to the surface of roll 13. This film is then brought into contact with the travelling sheet or web of paper, and transferred onto the sheet in the same uniform condition in which it was formed on the surface of the roll, thereby forming a complete, continuous and uniform film upon the sheet of paper. The thickness is regulated by the spacing between rolls 13 and 14 which provides for accurate control of the film applied from a heavy coating to a very thin coating.

The coating applied in this manner is found to be highly satisfactory, and to provide a uniform, homogeneous, and impervious upper surfacing over the lower coating layer, avoiding the formation of a spotty or irregular surface coating.

The upper coating composition may be such that it requires a period of drying before the coated web is rolled up or sheeted or otherwise handled. In this event, the coated web can be passed through a drying tunnel supplied with adequate heat and ventilation or can be passed over heated drying rolls or the like. Where the upper coating composition contains a volatile solvent, for example, the solvents accompanying the cellulose ester solution, temperatures of 140 to 200° F., or thereabouts, in the drying tunnel will be adequate.

The invention thus provides for the application to a sheet of paper of coatings having desired characteristics of greaseproofness and of waterproofness, and flexibility, forming a coated paper material especially desirable for use in the manufacture of containers for receiving oils and greasy materials, paints, turpentine, and the like. The flexible characteristics of the coating are such that the impervious character of the film is maintained through the necessary forming operations, and throughout the use of the formed container, without incurring rupture or damage to the impervious character of the film in the normal use of containers formed therefrom.

While the process and article herein described constitute preferred embodiments of the invention, it is to be understood that the invention is not limited to this precise process and article, and that changes may be made therein without departing from the scope of the invention which is defined in the appended claims.

What is claimed is:

1. A method of forming a substantially waterproof and greaseproof sheet of paper which comprises applying to the surface of a sheet of paper a lower surface coating layer including a water soluble adhesive from the group consisting of glue, casein, soy bean flour, and proteins derived from soy bean flour, and a plasticizing agent therefor adapted to maintain said coating in a flexible condition, applying a hardening agent comprising formaldehyde to said lower coating layer, thereafter forming a smooth uniform film consisting essentially of a solution of resinous material in an organic solvent of a character adapted to wet the surface of the lower coating, and transferring such preformed smooth surface film of resinous material onto said coated sheet of paper in homogeneously bonded and adhering relation thereto to provide a coated sheet having the upper coating layer uniformly and homogeneously distributed over and keyed into said lower coating layer so as to be jointly flexible therewith.

2. A method of forming a substantially waterproof and greaseproof sheet of paper which comprises applying to a sheet of paper a lower surface coating layer including an aqueous solution containing approximately 250 parts of water, 100 parts dry animal glue and up to 230 parts of sorbitol as a plasticizing agent therefor adapted to maintain said coating in a flexible condition, applying a hardening agent, and applying an overlying surface coating consisting essentially of a resinous material and a solvent of a character adapted to wet the surface of the lower

coating and to cause said overlying coating to key into said lower coating such as to be jointly flexible therewith.

3. A method of forming a substantially water-proof and greaseproof sheet of paper which comprises applying to a sheet of paper a lower surface coating layer maintained as a film on the surface of the sheet and including a water soluble glue and a plasticizing agent therefor adapted to maintain said coating in a flexible condition, applying a hardening agent, and applying an overlying surface coating consisting essentially of a resinous material and a solvent therefor containing alcohol and substantially free of hydrocarbons adapted to wet the hardened surface of the lower coating film to cause said overlying coating to key into and become intimately bonded with said lower coating so that it becomes jointly flexible therewith.

4. A method of forming a substantially water-proof and greaseproof sheet of paper which comprises applying a lower surface coating to a sheet of paper containing a water soluble glue and a plasticizing agent therefor adapted to maintain said layer in a flexible condition, forming a smooth uniform film consisting essentially of a solution of resinous material in an organic solvent of a character adapted to wet the surface of the lower coating, and transferring such preformed smooth surface film of resinous material onto said coated sheet of paper to provide a composite coated sheet having the upper coating layer uniformly and homogeneously distributed over and keyed into said lower coating layer.

5. A sheet of paper having a composite greaseproof coating thereon comprising the lower surface coating layer applied to the surface thereof as a heated emulsified mass including an aqueous solution of plasticized animal glue as the continuous phase, and a tacky solution in organic solvents of a resinous material as the dispersed phase, said surface coating layer upon cooling being in the form of a flexible surfacing film, and an overlying coating film consisting essentially of a resinous material upon said lower coating layer intimately bonded through wetting solvent action thereto and forming a composite flexible greaseproof surfacing for said sheet of paper.

6. A sheet of paper having a composite greaseproof coating thereon comprising a lower surface coating layer applied as a heated emulsified mass including an aqueous solution comprising of the order of 9 parts of water with 1 to 3 parts of plasticized glue as the continuous phase, and a solution of a synthetic alkyd resinous material as the dispersed phase, said surface coating layer upon cooling being in the form of a flexible surfacing film, and an overlying coating film consisting essentially of a resinous material upon said lower coating layer intimately bonded

through wetting solvent action thereto and forming a composite flexible greaseproof surfacing for said sheet of paper.

7. A method of forming a substantially water-proof and greaseproof sheet of paper which comprises applying a lower surface coating to a sheet of paper containing a water soluble glue and a plasticizing agent therefor adapted to maintain said layer in a flexible condition, hardening said surface coating by application of formaldehyde thereto, forming a smooth uniform film consisting essentially of a solution of resinous material in an organic solvent of a character adapted to wet the surface of the lower hardened coating, and transferring such preformed smooth surface film of resinous material onto said hardened coated sheet of paper to provide a composite coated sheet having the upper coating layer uniformly and homogeneously distributed over and keyed into said lower coating layer.

8. A method of forming a substantially water-proof and greaseproof sheet of paper which comprises applying a lower surface coating to a sheet of paper containing a water soluble glue and a plasticizing agent therefor adapted to maintain said layer in a flexible condition, forming a smooth uniform film consisting essentially of a solution of resinous material from the group consisting of phenol and urea formaldehyde resins, glyptal resins prepared from polyhydric alcohol and phthalic anhydride, vinyl resins, alkyd resins, and chlorinated rubber in an organic solvent of a character adapted to wet the surface of the lower coating, and transferring such preformed smooth surface film of resinous material onto said coated sheet of paper to provide a composite coated sheet having the upper coating layer uniformly and homogeneously distributed over and keyed into said lower coating layer.

9. A sheet of paper having a composite greaseproof coating thereon comprising the lower surface coating layer applied to the surface thereof as a heated emulsified mass including an aqueous solution of plasticized animal glue as the continuous phase, and a tacky solution in organic solvents of a resinous material as the dispersed phase, said surface coating layer upon cooling being in the form of a flexible surfacing film, and an overlying coating film consisting essentially of a resinous material from the group consisting of phenol and urea formaldehyde resins, glyptal resins prepared from polyhydric alcohol and phthalic anhydride, vinyl resins, alkyd resins, and chlorinated rubber upon said lower coating layer intimately bonded through wetting solvent action thereto and forming a composite flexible greaseproof surfacing for said sheet of paper.

HARRY C. FISHER.
JAMES F. THOMPSON.
WALTER E. SOOY.