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PAPER SIZED WITH FLUOROCARBON AGENTS ON ONE SIDE AND COATED ON THE OPPOSITE SIDE WITH THERMOPLASTIC MATERIALS

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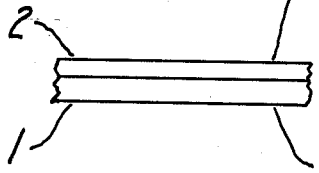

WATER-INSOLUBLE THERMOPLASTIC COATING (e.g., WAX OR ASPHALT) APPLIED FROM HOT MELT ON UNTREATED SIDE OF PAPER

POROUS PAPER TREATED ON BACK SIDE ONLY WITH OLEOPHOBIC FLUOROCARBON SIZING AGENT (e.g., CHROMIUM COMPLEX OF FLUOROCARBON MONOCARBOXYLIC ACID)

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PAPER SIZED WITH FLUOROCARBON AGENTS ON ONE SIDE AND COATED ON THE OPPOSITE SIDE WITH THERMOPLASTIC MATERIALS

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This invention relates to new and useful coated papers of the type made by coating a porous paper on one side with a hot-melt application of a water-insoluble thermoplastic material, such as a wax, or a waxy composition, or an asphalt.

The invention provides novel coated papers characterized by the fact that an initially unsized porous paper is treated on one side only (constituting the back side of the product) with an oleophobic fluorocarbon sizing agent (e.g., a chromium complex of a fluorocarbon monocarboxylic acid), in amount which does not appreciably change the porosity of the paper, and is subsequently coated on the other (untreated) side with a water-insoluble thermoplastic coating composition (e.g., wax or asphalt) applied from a hot melt, which does not objectionably strike through the paper as it would have if the paper had not been sized.

The accompanying drawing is a schematic edge view of the aforesaid coated paper product, showing the back sized paper 1 carrying the thermoplastic coating 2 on the untreated side.

The invention permits of employing porous papers of such light weight or openness that application of the hot-melt coating composition to one side would, in the absence of the special pre-treatment of the paper that we utilize, result in the coating composition striking through to the back side of the paper by flowing through pinholes and other passageways that are inevitably present. Such penetration is undesirable not only for the sake of appearance but because fouling of the back surface of the paper seriously interferes with utility in many cases, as by causing the back of the paper to adhere to or contaminate or dirty other surfaces which may subsequently make contact with the thus exposed coating material, or by interfering with printing or gluing of the back of the paper or its lamination to another sheet or article.

Papers coated on one side with a thermoplastic material are employed for many purposes. Wax-coated and asphalt-coated papers are employed as wrappers and liners, the wax or asphalt coating providing a barrier to moisture and water, and these papers are frequently laminated to another paper or to a foil or a film. Another example is adhesive sheets and tapes made of paper coated on one side with a thermoplastic adhesive composition. Still another example is carbon paper formed of a thin paper coated on one side with a waxy carbonizing dope or ink composition, used for making carbon copies. The present invention permits of using less expensive paper, and of using paper which is superior in one or more respects, as compared to the type of paper that otherwise would be needed.

In the case of carbon papers it is especially desirable to be able to use as thin and flexible a paper as possible so as to maximize the number of legible copies that can be made at one time, but it is essential that the carbon ink not strike through the paper as this would result in dirtying the backs of the writing papers used in conjunction when making manifold copies or typewriter copies.

The application of a barrier coating to the paper to prevent penetration is not a satisfactory solution of the problem because such coatings materially affect the thickness and flexibility of the carbon paper and hence reduce the number of legible copies that can be made at one time. The papers heretofore employed have been made from highly-beaten, highly-hydrated sulfite fibers, similar to glassine-paper stock, and these papers have been similar to glassine paper except that they are not super-calendered; the object being to provide sufficient body, density and continuity in a relatively thin and flexible paper (tissue paper) to avoid penetration by the applied hot-melt carbon ink composition. These papers are inherently substantially greaseproof and depend upon this characteristic.

We have made the surprising discovery that penetration by the hot-melt coating composition of porous papers that are not inherently of the grease-resistant type, can be prevented by pre-treating the porous paper on the back side with an oleophobic fluorocarbon sizing agent applied to the surface of the paper as a suitably dilute solution or dispersion in a volatile liquid vehicle so that, upon drying, the back side is rendered oleophobic. The individual paper fibers are sized and there is no appreciable change in the initial porosity, flexibility and thickness of the paper. The oleophobic fluorocarbon sizing agent does not penetrate sufficiently to the front (untreated) side of the paper to render the latter similar to the treated side, the two surfaces differing in kind and not merely in degree. Application of the hot-melt coating composition to the untreated front side of the paper in the usual manner results in a well-bonded coating without any strike-through to the back surface of the paper even though a paper has been utilized which otherwise would be unsuitable because of strike-through.

This discovery was surprising because it had been assumed that the logical procedure would be to apply the hot-melt coating to the side of the paper that had been given the oleophobic sizing treatment to thereby prevent penetration owing to the inability of liquid wax, asphalt, and the like, to wet an oleophobic surface. The assumption had been made that the oleophobic fibers would prevent capillarity and consequent penetration into and through pinholes and other passageways. On the other hand, if the hot-melt coating composition were to be applied to the untreated side of the paper, it would be a logical assumption that penetration could occur much more readily. Contrary to expectation, it was ultimately discovered that a much superior resistance to penetration occurs when the hot-melt composition is applied to the untreated side of the paper rather than to the treated side. The difference in behavior is so great as to permit of using papers having a degree of openness and porosity that would not permit of satisfactory use were the hot-melt coating composition to be applied to the treated side of the paper. And even in the case of papers that might be coated in the latter manner with reasonably satisfactory results, the present procedure is advantageous in ensuring against pinhole penetration and thereby improving quality.

A consequential desirable feature of the present invention is that the back surface of the coated paper has not only a highly oleophobic nature but also a highly hydrophobic nature, due to the fact that coatings of oleophobic fluorocarbon sizing agents are inherently hydrophobic. Thus the back side of the coated paper is rendered resistant to water and aqueous media as well as to oily and greasy materials. In the case of papers coated with wax or asphalt and used as wrappers or liners, or as laminates in combination wrappers and liners, this is an important feature. Contact of the paper with liquid water will not cause the exposed paper to lose strength

or become damp or wet. Contact with oily or greasy materials will not result in penetration of the paper to soften or permeate the wax or asphalt coating on the reverse side of the paper.

A further advantage of the fluorocarbon back sizing is that the back surface of the coated paper has a much lesser tendency to adhere or stick to the coating material which it contacts when the paper is stacked in sheets or is rolled upon itself. Moreover, the hot-melt coating composition is applied to a paper surface which readily absorbs the composition in its liquid state, resulting in a tenacious anchorage and bonding to the paper fibers by the ultimate solid coating of the finished product.

A very important advantage of using a paper sized on one side only with the oleophobic fluorocarbon sizing agent is that the treatment cost can be materially reduced as compared with the cost when the paper is sized or impregnated from both sides with the minimum effective amount of sizing agent. This is a very material factor in respect to economic feasibility and utility owing to the relatively high cost of these fluorocarbon sizing agents. We have discovered that the effective minimum amount of sizing agent that can be employed in practicing our invention is of the order of one-half the effective minimum amount required when the same paper is sized from both sides to proof it against strike-through of hot-melt wax or asphalt coating materials.

Oleophobic fluorocarbon sizing agents are already known to the paper sizing art and are available from Minnesota Mining & Manufacturing Company (St. Paul, Minnesota). These compounds as a class are carbon compounds which are chemically characterized by having in the molecule one or more highly fluorinated or perfluorinated terminal chains or side chains serving as fluorocarbon "tails." This "tail" is both oleophobic and hydrophobic, in contrast to a hydrocarbon chain, which is oleophilic. The molecule also includes one or more hydrophilic polar groups which serve to solubilize a portion of the molecule and which also serve to bond the molecule to hydrophilic surfaces when the compound is coated on such a surface. A polymeric molecule will include a large number of fluorocarbon "tails."

The sizing compound is applied as a dilute solution in water or a volatile organic solvent and upon drying a minute coating is provided upon the hydrophilic substrate fiber surfaces. Due to orientation of the molecules, the coating is tenaciously bonded and the outer surface of the coating has a fluorocarbon-like characteristic that renders it both hydrophobic and oleophobic. In sizing porous paper, the individual paper fibers can be coated and rendered highly hydrophobic and oleophobic without materially affecting the porosity of the paper. Capillarity can thereby be prevented both as to water and oil and as to molten thermoplastic materials such as wax and asphalt.

Preferred oleophobic fluorocarbon paper sizing agents are the chromium coordination complexes of fluorocarbon monocarboxylic acids. These acids have a carboxylic acid group at one end of the molecule and a fluorocarbon "tail" at the other end, this "tail" preferably consisting of 5 to 10 fluorinated carbon atoms. These complexes can be readily prepared by reacting the fluorocarbon acid (e.g., perfluorocaprylic acid, $C_7F_{15}COOH$) with chromyl chloride in an isopropanol vehicle which serves both as a solvent and as a reducing agent, a suitable mole ratio being 3 moles of chromyl chloride per mole of fluorocarbon acid. Volatile side-products can be removed by distillation. The green-colored isopropanol solution of the chromium complex is diluted with water at time of use to provide a sizing solution containing a few-tenths of a percent or less of the chromium complex. A neutralizing agent (such as urea) can be included to neutralize HCl that is evolved when the applied sizing coating is dried and heated to insolubilize and polymerize the chromium complex. Chromium

complexes of this type are described in U.S. Patent No. 2,662,835 (Dec. 15, 1953). The chromium complex of perfluorocaprylic acid can be employed in minimum effective amounts of about 0.05 to 0.5% by weight in the paper (dry sizing weight) in practicing the present invention, the amount required depending upon the kind of paper and upon the particular kind of hot-melt thermoplastic coating material and the coating conditions.

Another illustration of an effective sizing agent is provided by the polymers of acrylate and methacrylate esters of fluorocarbon alcohols. These alcohols have an alcohol group ($-CH_2OH$) at one end of the molecule and a fluorocarbon "tail" at the other end, this "tail" consisting of three or more fluorinated carbon atoms. The ester monomers can be polymerized in aqueous dispersion to provide an aqueous latex of the polyacrylate or polymethacrylate, which can be diluted with water and used as a paper sizing. Fluorocarbon polymers of this type are described in U.S. Patents Nos. 2,642,416 (June 16, 1953) and 2,713,593 (July 19, 1955).

The paper to be sized in accordance with the present invention can be conveniently treated by passing between a pair of rotating horizontal squeeze rolls, the lower roll having a resilient rubber covering and being partially immersed in the sizing solution so as to transfer the latter to the lower side of the paper. The wet coating weight can be adjusted by regulating the pressure between the squeeze rolls so as to squeeze out excess solution. Other well-known procedures can be used to apply the solution to one side of the paper, such as by means of a spray, size press, reverse roll, knife coater, air knife, etc. The paper is then dried by passing around one or more steam-heated can driers or calender rolls in such manner that the untreated side of the paper contacts the heated metal surface.

Since the porous paper is initially unsized, the sizing solution is absorbed from the surface to which it is applied, but in passing through the body of the paper the sizing compound is progressively removed by adsorption on the paper fibers. By using a sufficiently dilute sizing solution and regulated wet coating weight, the pentration of the sizing solution can be controlled to produce a concentration gradient of the sizing agent solids relative to the paper, the concentration decreasing in the direction of the reverse side of the paper. The concentration of sizing agent solids at the treated surface is approximately double the average value for the entire paper cross-section, when the sizing agent is employed in an economically optimum amount.

The disparity between the treated and untreated sides of the paper can be easily demonstrated by a simple test. A piece of the paper is dipped into a glycerine bath and promptly removed. The glycerine will not have wetted the sized side of the paper and it literally rolls off, leaving a substantially dry surface. However, it will have wetted the untreated side of the paper and this side of the paper will be seen to be wet with glycerine which the paper absorbs, as further indicated by the darkened appearance of the wet paper fibers. The treated side of the paper has been rendered repellent to glycerine but not the untreated side. This glycerine test correlates so well that it can be employed in determining the approximate conditions for the one-side sizing treatment of any given paper to obtain the economically optimum treatment that is effective; sample sheets being sized with solutions of differing concentrations and being tested with glycerine after drying.

As previously indicated, the present invention has particularly notable utility in the manufacture of carbon papers. It has been found, for example, that a light weight porous kraft paper, made from pulp beaten to a Canadian Standard Freeness of about 300 ml., having a ream weight of 10 pounds (weight of 3,000 square feet), can be sized on one side with a fluorocarbon chromium complex sizing agent at a solution concentra-

tion of 0.2% by weight (producing a dry sizing weight of 0.15% of the paper weight), followed by drying at 200–230° F., to produce a sized paper that can be coated with molten carbon "dope" (waxy carbon ink) on the untreated side without strike-through. The paper had a caliper thickness of 1.2 mils and the product had a thickness of 1.7 mils. The utilized chromium complex had been made from chromyl chloride and perfluorocaprylic acid in 3:1 mole ratio. The resulting carbon paper is thinner than a conventional carbon paper made from highly-beaten sulfite stock and weighing 15 pounds per ream, and tests show that a greater number of legible simultaneous copies can be made. When the sized paper was coated on the treated (sized) side with the carbon dope, for comparison, the product was unusable owing to strike-through of the ink. Comparative carbon papers made with the same paper but saturated from both sides with sizing solution, showed that strike-through avoidance required a solution concentration which was also 0.2% by weight but which resulted in a dry sizing weight in the paper of 0.25% (in contrast to an effective dry sizing weight of 0.15% when one-side sizing was used).

In other tests, a 15 pound per ream unbleached kraft paper, made from pulp beaten to a Canadian Standard Freeness of about 400 ml. and similarily sized, was coated on the untreated side with molten paraffin wax without strike-through. The paper had a caliper thickness of 2.0 mils and the product had a thickness of 3.0 mils, the coating weight of the wax being 15 pounds per ream. In contrast, when the wax was applied to the treated side of the paper considerable penetration occurred, which rendered the reverse side unsuitable for printing or gluing.

An excellent asphalt coated paper was made by coating molten asphalt (No. 8 coating asphalt having a melting point of about 125° C.) on a similarly sized 30 pound per ream unbleached kraft paper made from a pulp beaten to a Canadian Standard Freeness of about 500 ml. Resistance to bleeding through of the asphalt was further demonstrated by laminating together two sheets of asphalt-coated paper, forming a sandwich with the asphalt on the inside, and hanging vertically in an oven having an air temperature of 125° C. Observations were made at intervals during a ten minute test period. There was good resistance to pinhole strike-through. Poor results were obtained in comparisons employing paper which had been coated with asphalt on the treated side.

The Canadian Standard Freeness values referred to above were obtained by a procedure conforming substantially to TAPPI Standard T205*m*–53 (a published test method of the Technical Association of the Pulp and Paper Industry). The freeness test is an empirical one that gives a measure of the rate at which a paper-making pulp can be dewatered. Highly-beaten highly-hydrated pulps have a low value. For instance, pulps used in making conventional carbon papers may have a value of 50–10 ml. A high freeness value (e.g., 300–500 ml.) makes for a relatively open paper and one prone to pinholes and hence not normally suited for coating with hot-melt thermoplastic compositions when strike-through is objectionable.

Tests have been made using a variety of different fluorocarbon sizing agents and have confirmed the general effectiveness thereof and the advantages (both technical and economic) of sizing the paper on one side and applying the thermoplastic coating material to the other side, as compared with applying the coating material to the treated side and also as compared with applying the coating material to one side of paper that has been sized on both sides.

We claim:

1. As a new article of manufacture, an initially porous unsized paper that has been fiber sized on one side only with an oleophobic fluorocarbon sizing agent in amount which does not appreciably change the porosity of the paper and which renders the treated side of the paper repellent to glycerine but not the untreated side, and that has been subsequently coated upon the untreated side with a coating of a water-insoluble thermoplastic coating composition applied from a hot-melt and which does not objectionably strike through the paper as it would have if the paper had not been sized.

2. A coated paper according to claim 1 wherein said coating is a wax coating.

3. A coated paper according to claim 1 wherein said coating is an asphalt coating.

4. A coated carbon paper according to claim 1 wherein said coating is a waxy carbon ink coating.

5. A coated paper according to claim 1 wherein said sizing agent is a chromium coordination complex of a fluorocarbon monocarboxylic acid having from 5 to 10 fluorinated carbon atoms in the molecule.

6. A carbon paper of the character described, comprising an initially porous unsized light-weight kraft paper made from a pulp beaten to a Canadian Standard Freeness of 300 to 500 ml., that has been fiber sized on one side only with an oleophobic fluorocarbon sizing agent in amount which does not appreciably change the porosity of the paper and which renders the treated side of the paper repellent to glycerine but not the untreated side, and that has been subsequently coated upon the untreated side with a waxy carbon ink applied from a hot melt and which does not strike through the paper as it would have if the paper had not been sized.

7. A carbon paper according to claim 6 wherein said sizing agent is a chromium coordination complex of a fluorocarbon monocarboxylic acid having from 5 to 10 fluorinated carbon atoms in the molecule.

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