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DENSE PAPERS AND PROCESS FOR PREPARING THEM

Alfred H. Nadelman, Kalamazoo, Mich., assignor to Allied Chemical Corporation, a corporation of New York

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This invention relates to papers of high density and more particularly to high density glassine papers of greatly enhanced resistance to penetration of gases and greases and to a process for preparing them.

Glassine paper has been produced in the past by first forming a highly hydrated chemical wood paper such as sulfite pulp paper, known as "greaseproof" paper, then adding moisture to such paper to the extent of up to about 50%, usually between about 20% and about 30% of its total weight, and subjecting the moist sheet to supercalendering.

The resulting glassine paper is a thin, translucent, dense paper having a considerable degree of grease and gas penetration resistance, and finds wide use in protecting food products, for example, in lining cereal and cracker cartons, in candy boxes, candy cups, etc., and has numerous other well established uses.

While the grease and gas resistance of conventionally prepared glassine papers is considerably higher than that of ordinary book or bond paper, such papers often contain imperfections such as thin spots or so-called "pin holes" which cause small areas to be permeable to gas and grease in a sheet otherwise highly resistant to these factors, so that adequate means for curing such imperfections so as to enhance the overall grease and gas resistance of the sheet would be highly desirable.

It is known to apply solvent coatings or aqueous dispersions of waxes to papers to improve their moisture resistance or to improve their gloss or calendering properties. Such coatings, however, while increasing the moisture resistance, result in very little, if any, increase in grease resistance since many of the waxes customarily used for coating papers are either soluble in, or softened by the commonly encountered oils.

It is an object of the present invention to provide high density papers, and a process for preparing them.

It is another object of the invention to provide a glassine paper of greatly enhanced grease resistance.

A further object is to provide a process for preparing a highly grease resistant glassine type paper which process can be carried out on the regular equipment commonly used in glassine production and with no additional process steps.

A still further object of my invention is to provide a process for treating glassine paper which not only greatly enhances its grease resistance, but which also improves its resistance to permeation by air and other vapors including water vapor.

Another object is to provide a glassine paper of greatly enhanced density characteristics.

These and other objects are accomplished according to my invention, wherein highly hydrated chemical pulp papers such as conventional "greaseproof" or other highly hydrated papers are treated with an aqueous emulsion of an oxidized polyethylene wax as hereinafter defined, and are thereafter supercalendered wet in the manner conventional in the manufacture of dense papers.

In carrying out the process according to my invention, an aqueous emulsion of the oxidized polyethylene wax is applied to the paper by any convenient method of application, adapted to apply the required amount of emulsion to the sheet and to assure its absorption into and onto the fibers of the sheet. If desired, an excess of emulsion may be, and usually is, applied, and this excess is removed by suitable treatment after application such as passage through squeeze rolls or the like. The emulsion treated sheet may then be "wet calendered" immediately, but preferably will be reeled after treatment with emulsion, wrapped in a moistureproof wrapping and held for a sufficient time to insure uniform penetration of the impregnating emulsion.

The treated paper is then wet calendered on heated rolls in the manner customarily used in calendering to produce dense papers such as glassine paper, e.g., in a multi-roll super-calender stack, containing for example, from 9 to 20 rolls, usually of alternating chilled iron and compressed paper rolls, but which may have two or more adjacent paper rolls, and having their roll surfaces heated to between about 150° F. and about 270° F., depending on speed of operation. Calendering is effected under pressures usually equivalent to between about 2,000 and about 7,000 p.s.i. at the calender nip, which simultaneously compresses, smooths and dries the paper.

The resulting papers have greatly increased densities as measured by specific gravity, usually being greater than 1, for example, at least about 1.05, often as high as 1.2 or more. Density of papers is more often expressed in terms of "porosity," for example, as measured by the Gurley "densometer" in which the results are reported in number of seconds required for 100 ml. of air to pass through one square inch of paper. When measured in this manner, the treated papers of my invention may have densities up to 10 times, i.e. 1,000% as great as those of the original untreated paper, and up to 4 times, i.e. 400% as great as finished papers, such as glassine, prepared from the same rawstock according to conventional procedures for preparing glassine papers for example about 30,000. This reduction in gas permeability greatly enhances the value of the papers for uses in protecting products from contact with air or other gases, for example, in food packaging and the like.

When "greaseproof" grade of paper has been used as the rawstock, the resulting sheet is a dense glassine paper having the desirable properties of ordinary glassine plus improved gloss and greatly enhanced density and grease resistance, the latter characteristic being partly a function of the density, partly a function of relative freedom from imperfections such as "pin holes," etc. and depending to some extent on the oil or grease to which the paper is exposed. Thus, as compared to glassine papers finished by wet calendering alone without addition of oxidized polyethylene wax, the same papers treated in accordance with my invention may show grease resistance characteristics, for example, as much as 15 times, i.e. 1500% as great against mineral oil, 6 times or 600% as great against oleic acid, and up to 3 to 4 times or 300 to 400% as great against the extremely strongly penetrating turpentine for instance, between about 90 and about 120 as measured by TAPPI Standard T–45m–44.

Greatest improvements in both density and grease resistance will, of course, result when my treatments are applied to the lower grades of greaseproof papers, i.e., those which if processed to glassine, would have relatively low greaseproof characteristics and relatively high gas permeability or porosity characteristics. Thus, my invention provides a means for up-grading such lower grades and bringing them into higher categories of usefulness.

Papers suitable for treatment according to my invention to produce dense papers include any of the highly hydrated cellulosic papers, for example, chemical or semichemical wood pulp papers, particularly coniferous wood pulp papers such as sulfite or sulfate pulp, hydrated so as to have a freeness as it enters the paper machine of not more than about 300 ml. as measured by the standard Schopper-Riegler freeness tester, preferably papers made from pulps having freenesses by the above method between about 250 ml. and about 150 ml. So-called "greaseproof" papers are especially suitable for treatment according to the invention. The so-called "greaseproof" papers are papers prepared from unfilled sulfite and sulfate pulps which are highly hydrated by mechanical action alone (as distinct from chemical treatment) in the presence of water, as by beating, jordaning, etc., and after formation, are machine calendered. They are distinguished from other grades of unfilled sulfite papers such as the so-called "waxing" papers by the higher degree of hydration of the pulps from which they are made, and are thus adapted, on wet-supercalendering, to produce dense papers having a high degree of transparency. Thus, the so-called "greaseproof" papers are usually prepared from unfilled sulfite and sulfate pulps having freeness characteristics, as they reach the paper machine, between about 300 ml. and about 150 ml., whereas "waxing" papers are usually prepared from pulps having freeness characteristics of at least about 500 ml. by the above test, as they enter the paper machine.

The method of applying the oxidized polyethylene wax emulsion is not critical, and any suitable convenient method of application may be employed. Good results are obtained by immersing a travelling web of paper in the emulsion followed by passage of the web through squeeze rolls, using the well known "tub sizing" technique. Alternatively, the emulsion may be applied by a roll or brush rotating partially submerged in a trough of the emulsion to pick up a layer of emulsion and transfer it either directly or by intermediate means to the paper, or even by direct application at the nip of two rolls through which the paper passes. Usually an excess of emulsion will be applied initially, and the excess above that required to apply the desired proportions of solids and moisture, will be removed.

The oxidized polyethylene wax is preferably applied so that as large a portion of the total solids as feasible will penetrate the pores of the paper, although a small portion remaining on the surface of the paper will do little harm.

The quantity of oxidized polyethylene wax applied is not unduly critical. Even small quantities may produce significant enhancement of the density and grease resistance characteristics of the resulting glassine papers, particularly those of proorer grades. In general, I find it desirable to deposit at least about 0.5% of oxidized polyethylene wax, based on the weight of the paper, and sufficient to insure the desired increase in density and in the resistance to penetration of gases and the various greases. In general, between about 0.5% and about 8% of the oxidized polyethylene wax based on the weight of the bone dry paper may readily be applied, preferably between about 2% and about 6%.

In any event, the emulsion will be applied so as to deposit the requisite amount of oxidized polyethylene wax and also to impregnate the paper to a uniform moisture content usually between about 20% and about 30%; sometimes as high as 50% as is customary in the well known procedures for making glassine paper.

The amount applied can be varied somewhat by adjusting the solids concentration of the emulsion and by varying details of the method of application by procedures within the skill of the art. Suitable wax concentrations in the emulsion may be between about 10% and about 40%, preferably between about 12% and about 20% to produce emulsion viscosities adapted to paper treating techniques and the deposition of adequate quantities of solids to effect the desired enhancement in density and grease resistance.

The oxidized polyethylene wax suitable for use in the process of the invention may be one having a molecular weight between about 1,000 and about 5,000. It may be prepared according to the process of copending application Serial No. 515,770, of Michael Erchak, Jr., or Serial No. 524,620, of Wilbur F. Chapman and John Cosby. Especially suitable are those obtained by oxidizing polyethylene/isopropanol telomer waxes having average molecular weights between about 1,000 and about 5,000 and containing between about 2% and about 7% oxygen, and a ratio of saponification number to acid number of not more than about 1.5, preferably between about 1 and 1.2. These oxidized polyethylene waxes have superior hardness and toughness characteristics usually having penetration values not more than about 0.5 mm. as measured by Standard ASTM method D-5-25 and toughness values of at least about 2.0 foot pounds per linear inch as measured by Standard ASTM method D-256-47T, and are readily emulsifiable in water. The oxidized polyethylene wax emulsions may be prepared by any suitable method, using any suitable emulsifying agents, and the concentration of the oxidized wax solids may vary as required, to apply the predetermined amount of oxidized wax to the papers. A suitable oxidized polyethylene wax emulsion may be prepared, for example, by melting the wax, adding a small amount of fatty acid such as oleic acid, then, with melt temperature at say, 120-130° F., adding a small amount of an organic amine such as morpholine. The resulting molten mixture may be added with rapid stirring to hot (95-99° C.) water, at a steady rate to the top of the vortex formed by the stirring, the wax spiralling down the vortex and being emulsified therein. Other fatty acids such as stearic acid, etc., may be used, and other organic amines, including monoethanol amine, diethanol amine, triethanolamine, 2-amino-2-methyl-1-propanol, etc. as well as other suitable emulsifying agents.

Emulsions may be applied containing the oxidized polyethylene wax as the only effective solids constituent of the emulsion, or the emulsions may contain other additives particularly emulsified petroleum waxes such as paraffin wax or microcrystalline wax, etc.

The following specific example further illustrates my invention. Parts are by weight except as otherwise noted.

EXAMPLE

A roll of "greaseproof" paper 5½ inches wide of a character suitable for the preparation of glassine paper, and having physical characteristics shown in the table below, was divided into two equal portions which were processed to glassine paper by wet calendering, in identical manner except that the first portion was impregnated with water alone, the second with a 15.6% aqueous emulsion of oxidized polyethylene wax, each to the extent of 30% of the paper's original weight.

The oxidized polyethylene wax was an oxidized polyethylene/isopropanol telomer wax containing about 3% oxygen and having an average molecular weight about 1500. It was emulsified by melting 30 parts of the wax with 6 parts of morpholine, and adding the molten mixture with stirring to 138 parts of 95-99° C. water as described above.

Each web of paper was "tub sized" with treating liquid, i.e. was immersed in and passed through the treating liquid located in a tray adjacent the size press of a conventional Mayer coating machine, the web travelling at a speed of 8 ft. per minute. It was passed through the nip of two press rolls adjusted to insure a moisture content in the paper of about 25-30%. Both webs were wound into rolls immediately after passing through the press, placed in moistureproof bags and stored for sixteen hours to insure uniform penetration of the treating liquid and to maintain the desired moisture content for wet calendering.

The moist paper was then cut into sheets 9" x 5½" and calendered on a laboratory calender consisting of a pair of steel rolls and an intermediate filled paper roll, at a surface temperature of 155° F. and a pressure equivalent to 6,180 ps.i. at the nip. Each sheet was passed through the nip ten times to simulate the calendering operation in the production of commercial glassine paper.

The resulting calendered products were tested for gloss, brightness, opacity, porosity and grease resistance by the methods outlined below. Results of the tests are given in Tables I and II which also list the values of the above characteristics in the raw "greaseproof" stock prior to treatment.

Gloss was measured by a Photovolt 75 degree gloss meter according to TAPPI standard T-480m-51.

Brightness was measured on a standard Photovolt unit in terms of blue light reflectance as compared to a magnesium oxide standard.

Opacity was determined on a Photovolt opacity meter in terms of comparative reflectance from white and black backings.

Porosity was determined on a Gurley densometer according to TAPPI standard T-460m-49. Results are reported as the number of seconds required for 100 ml. of air to pass through one square inch of paper.

Grease resistance tests were made with turpentine according to TAPPI standard T-454m-44 and with lard, "Crisco" (hydrogenated cotton-seed oil), cocoa butter, oleic acid and mineral oil (all containing a red dye) by a modification of the above TAPPI test in which the specimen was placed on a horizontal surface and backed by a piece of white coated paper. Then, 0.25 gram of grease was placed on aluminum foil. The foil with grease was inverted onto the specimen, and a weight placed on top of the foil and allowed to remain for 5 seconds to create a uniformly smooth layer of the grease. Thereafter, a five gram portion of dry sand was placed on top of the foil to hold the specimen in firm contact with the coated paper. During the first two minutes of the test, the paper specimen was moved at 30 second intervals in order to observe whether or not spotting of the underlying coated paper had occurred. After the initial period more frequent additional observations were made. The results are reported as time in seconds elapsed to the appearance of the first red stain on the coated paper.

Table

Physical characteristic of glassine paper made with oxidized polyethylene wax emulsion

Characteristic	Paper		
	"Grease-proof" as received	Wet Calendered	Oxidized P.E. Treated and wet calendered
Basis Weight [a]	25.3	25.3	26.5
Caliper [b]	1.50	1.48	1.40
Density	1.078	1.092	1.210
Gloss:			
Felt side	30.8	33.0	36.6
Wire side	27.1	32.0	30.2
Brightness .... percent	62.2	57.5	46.0
Opacity	47.0	42.3	44.7
Porosity	2,316	7,417	29,860
Grease Resistance:			
Turpentine [c]	0	<30	108
Lard [d]	50	135	1,045
"Crisco" [d]	40	250	715
Cacao Butter [d]	[e] No spots	[e] No spots	[e] No spots
Oleic acid [d]	60	----------	360
Mineral oil [d]	152	----------	6,300

[a] 24 x 36—500.
[b] Thousandths of an inch.
[c] T-454m-44.
[d] Seconds for first spot to appear.
[e] After 600 minutes.

While the process has been described primarily as applied to "glassine" prepared from so-called "greaseproof" paper, it may be applied in similar manner to the manufacture of other dense paper specialties such as one-time carbonizing paper, condenser tissue, etc.

While the above describes the preferred embodiments of the invention, it wil be understood that departures may be made therefrom within the scope of the specification and claims.

I claim:

1. A process for increasing the density of a highly hydrated, chemical-pulp paper, which comprises incorporating into and onto the fibres thereof between about 0.5% and about 8% of an emulsifiable oxidized polyethylene wax having an oxygen content between about 2% and about 7% an average molecular weight between about 1,000 and about 5,000 and thereafter wet calendering the paper.

2. A process for increasing the density of a highly hydrated, chemical-pulp paper, which comprises applying thereto between about 20% and about 50% of its weight of an aqueous emulsion containing between about 10% and about 40% of an emulsifiable oxidized polyethylene wax having an oxygen content between about 2% and about 7% an average molecular weight between about 1,000 and about 5,000, and thereafter wet calendering the paper.

3. A process for producing a highly grease resistant glassine paper which comprises applying to "greaseproof" paper between about 20% and about 30% of its weight of an aqueous emulsion containing between about 12% and about 20% of an oxidized polyethylene wax having an oxygen content between about 2% and about 7% an average molecular weight between about 1,000 and about 5,000 and thereafter wet calendering the paper.

4. A process for producing a highly grease resistant glassine paper which comprises applying to "greaseproof" paper about 30% of its weight of a 12%–20% aqueous emulsion of an oxidized polyethylene wax having an oxygen content between about 2% and about 7% an average molecular weight between about 1,000 and about 5,000 and thereafter wet calendering the paper.

5. As an article of manufacture a dense, highly hydrated chemical-pulp paper sheet, having incorporated therein between about 0.5% and about 8% of an emulsifiable oxidized polyethylene wax having an oxygen content between about 2% and about 7% an average molecular weight between about 1,000 and about 5,000.

6. A process for increasing the density of a highly hydrated, chemical-pulp paper, which comprises incorporating into and onto the fibres thereof, between about 0.5% and about 8% of an emulsifiable oxidized polyethylene wax having an average molecular weight between about 1,000 and about 5,000 and containing between about 2% and about 7% oxygen.

7. A process for increasing the density of a highly hydrated, chemical-pulp paper, which comprises incorporating into and onto the fibres thereof, between about 0.5% and about 8% of an emulsifiable oxidized polyethylene/isopropanol telomer wax having an average molecular weight between 1,000 and about 5,000 containing between about 2% and about 7% oxygen and having hardness characteristics corresponding to penetration values of not more than about 0.5 mm. as measured by Standard ASTM method D-5-25, and toughness of values of at least about 2.0 foot pounds per linear inch as measured by Standard ASTM method D-256-47T.

8. As an article of manufacture a glassine type paper comprising a highly hydrated chemical-pulp paper sheet, having incorporated therein between about 0.5% and about 8% of an emulsifiable-oxidized polyethylene/isopropanol telomer wax having an oxygen content between about 2% and about 7%, and an average molecular weight between about 1,000 and about 5,000, said sheet having a porosity value, as measured by the Gurley densometer, of about 30,000, and a resistance to turpen-

tine penetration as measured by TAPPI Standard T-454m-44, of between about 90 and about 120.

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