Patented Dec. 26, 1939

2,184,307

UNITED STATES PATENT OFFICE

2,184,307

MANUFACTURE OF PAPER

Louis Leonard Larson, Wilmington, Del., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application September 28, 1936, Serial No. 103,049

2 Claims. (Cl. 92—21)

This invention relates to paper, more particularly to a grease-resistant paper, still more particularly to a process for sizing paper, and still more particularly to a process for producing impervious paper in the primary paper making operation.

In the paper making art there are two general methods of imparting grease resistance to paper. In one of these methods grease resistance is obtained by forming a sheet from special pulp which has been beaten exhaustively to a very slow, gelatinous state. This mechanical method is costly because a special pulp is required, power consumption is high, and the conversion rate is low in comparison with grades of paper made from freer pulps. Glassine paper is an example of grease-proof paper made from highly beaten pump. Various chemical methods are also known. In general, these consist in applying to the formed sheet strong parchmentizing reagents such as sulfuric acid, mercerizing caustic, zinc chloride, etc. These chemical methods are also costly because of the concentrated reagent required. They have the additional disadvantage that to obtain uniform results very close control is involved.

In the paper industry various size materials are incorporated by treatment of the furnish before sheet formation or by surface sizing the sheet at an intermediate stage in the drying operation or during the calendering operation. I find, however, that neither beater sizing nor surface sizing, using known systems of application, is capable of effecting a high degree of grease-proofness when the size is applied to free paper stock and when only non-parchmentizing reagents are used.

In the application filed by W. J. Merrill, Serial No. 89,254 filed July 6, 1936, a process has been disclosed whereby a grease-proof paper is produced by a combination of beater size and surface size, the latter being applied in a secondary process after the sheet is dried. I have now discovered a greatly improved and more economical process whereby an even greater degree of grease-proofness is obtained without any secondary operation, the special treatments which produce the grease-proofness taking place entirely within the primary paper making operation.

By the novel process described in this application, practically any desired degree of grease-proofness may be imparted to paper using paper pulp of any desired grade and using only comparatively dilute reagents under conditions which do not involve parchmentizing the cellulose fiber.

An object of this invention is in the production of an impervious paper by treatment with chemicals in the primary paper making operation. Another object is the production of paper in the primary paper making operation that is grease-proof, water-proof, and has high wet strength. A further object is to provide a process for producing grease-proof paper in the primary paper making operation which is not limited to light weight papers and which may be practiced with any paper pulp. A still further object is the production of grease-proof paper by using paper pulp which is freer than the highly beaten grease-proof pulps, thereby permitting the paper machine to operate at higher speeds. Other objects will appear hereinafter.

These objects are accomplished by the following invention: In a standard paper making operation which includes stock preparation, sheet formation, pressing, and drying in a continuous operation, the added steps which comprise (1) mixing the paper pulp with a size solution containing a film-former of the class specified below, (2) precipitating the size onto the paper pulp, (3) applying a swelling agent adapted to swell the precipitated size material, the point of application being sufficiently far forward toward the wet end of the machine, so that the swelling action is completed to the desired degree during the progress of the sheet through the machine, and (4) stopping the action of the swelling agent while the precipitated film-former is in a highly swollen state but before it has been dissolved to the sol state.

The film-forming materials of this invention are selected from those non-protein hydrophilic colloids which are soluble in aqueous media, which as 0.5% solutions are insoluble in aqueous media at a pH of 7.0 in the presence of a low concentration of a polyvalent ion, which are capable of laying down turpentine impermeable films from their aqueous solutions and which have a viscosity of not less than 2 poises as 5% aqueous solutions at 25° C.

Examples of these film-forming materials used in the size solution are carbohydrate polymers of the cellulose type such as acetic acid soluble deacetylated chitin and various alkali soluble cellulose derivatives including urea cellulose, cellulose ethers such as methyl and glycol celluloses, and cellulose glycolic acids.

Since the swelling reaction rate increases with concentration of agent, the concentration required to effect a given result is an inverse function of the available time. In general, the paper

maker will choose the minimum concentration which, under the fixed conditions, will effect the required results within the allowable time.

As swelling agent I use a material soluble in an aqueous medium which is capable, under conditions of use, of swelling the precipitated film-former but is not capable, under such conditions, of parchmentizing the cellulose fiber. The concentration of the swelling agent is adjusted with due regard to the time available for the completion of the swelling action.

An aqueous solution of a film-forming material which fulfills the requirements of the definition of the film-forming material that has been given herein, is added to and thoroughly mixed with paper pulp in a paper beater or any other suitable mixing device. The film-forming material is then precipitated in a finely divided state onto the fibers by adding a precipitating agent.

The next step in the process is to convert the precipitate of film-forming material into a highly swollen state by incorporating a swelling agent. This swelling agent may be added to the pulp or furnish at the head box or flow box just before sheet formation, or it may be added to the sheet at some point following sheet formation, the point of application being selected so that the swelling action may be completed during the passage of the sheet through the primary paper making operation. For a slow acting swelling effect, such as that obtained with deacetylated chitin, the paper maker will select the point of application on the forming wire in order to permit maximum machine speed. However, if this is undesirable, for example if the sheet is weak, a later point of application may be selected, providing the factors affecting rate of reaction, for example concentration, are adjusted so that the swelling action is completed within the time available.

The sheet dryness referred to herein represents the ratio of fibers (bone dry bases) to water and is obtained by pressing out water or by a combination of pressure and heat.

The swelling agent, which is incorporated as a water solution, is primarily an acid or a base depending upon whether the precipitated film-forming material is swollen by an acid or a base. However, in certain cases, it may be desirable to use as the swelling agent a combination of the acid or base with a film-forming material or some other modifying chemical which improves the swelling power of the acid or base.

The effect of the swelling agent is progressively reduced as the degree of sheet dryness is increased. Therefore the swelling agent should be applied at the point of maximum water content which is consistent with the time effect and operating ease, and its application should never be delayed until the sheet has been dried enough to wind into a satisfactory roll as dry paper.

It is important that both the concentration of the swelling agent in the sheet and the point of application of the swelling agent should be regulated carefully so that at the time the swelling action is stopped the precipitated film-forming material is in a highly swollen state, and preferably so that the swelling action has not proceeded beyond the optimum point as indicated by the turpentine resistance test made on the product. As a result of this swelling action and the subsequent pressing action, the film-forming material anchors thoroughly to the fibers and it also bridges between fibers so that during the subsequent drying process the pores of the sheet are closed.

The final step in the sizing process is to stop the action of the swelling agent while the film-forming material is in a highly swollen condition. This is done by part or complete removal of the agent through the application of heat to the sheet if the swelling agent is a volatile acid or base, or, if the swelling agent is non-volatile, by its neutralization. In the latter case, the neutralizing substance is subsequently removed from the sheet by washing baths. An important factor in this final step is the time allowed for the action of the swelling agent on the film-forming material. If this time of action is too short, insufficient swelling of the film-forming material results in low imperviousness of the dry sheet. If the time of action is too long, then a part of the film-former is converted to the sol state and the imperviousness of the sheet is lower. Thus, an optimum time of action exists and this optimum time depends upon the activity and concentration of the swelling agent. The action of the swelling agent should be stopped promptly when the optimum degree of swelling for maximum imperviousness has been effected.

From the materials known to the art, various size materials, solvents, precipitants, and swelling agents may be selected to meet the requirements mentioned above. Thus, the film-former may be deacetylated chitin dissolved in dilute acetic acid; the precipitant may be heat or an alkali; and the precipitate may be reswollen by dilute acetic acid. Another suitable system consists of low substituted methyl cellulose dissolved in dilute caustic soda, precipitated by sulfuric acid and the precipitate reswollen by dilute caustic soda or by a solution of methyl cellulose dissolved in caustic soda. Instead of the methyl cellulose, glycol cellulose may be used. Viscose may also be used as the size solution, precipitated by an acid coagulating bath and the precipitate then reswollen by prompt treatment with an additional amount of viscose solution. After coagulating the viscose, it is advisable to add the swelling agent promptly, that is, before the precipitate is largely converted to regenerated cellulose, and so that it can be reswollen without the use of a reagent sufficiently concentrated to parchmentize the fiber. In one preferred system, water-soluble sodium cellulose glycolate is used as the hydrophilic colloid. The glycolate solution may be neutral, acid, or alkaline. The precipitant is alum, which throws down the insoluble aluminum cellulose glycolate, and the swelling agent is a dilute solution of aqueous ammonia.

The following examples are given to illustrate the process of the invention without limiting its scope thereby.

Example I

This illustrates the production of an impervious sheet using deacetylated chitin as the film-forming material, acetic acid as the swelling agent, and heat to stop the action of the swelling agent. It also illustrates the influence of the concentration of the swelling agent on the swelling reaction rate and the variation of the imperviousness of the finished sheet with the degree of swelling of the precipitated film-former.

A ten-pound capacity beater was charged with a bleached Mitscherlich sulphite pulp (65–70% dry) at 3.9% fiber consistency, with the beater roll set to fibrillate without much cutting. The pulp was beaten until it was nine times as free as glassine paper pulp (77 seconds by the freeness

test described below). A portion of this pulp was sized in a one-half pound capacity beater as follows:

	Grams
3.9 per cent consistency pulp at 77" freeness	4000
Water	3500
1.25 per cent solution of deacetylated chitin in 0.375% acetic acid	398
1.00 per cent ammonium hydroxide solution	285

The solution of deacetylated chitin was mixed thoroughly with the pulp before addition of the ammonium hydroxide solution, which precipitated the deactylated chitin onto the fibers. This gave a deacetylated chitin content of 3.32% based on dry fiber weight. The pH of the sized pulp was 9.3. The freeness of the sized pulp was 74 seconds. Sheets were formed by regular procedure on a sheet mold, couched from the forming wire, and pressed to 40% sheet dryness (40 pts. fibers bone dry basis and 60 pts. water). At this point they were treated with acetic acid to swell the deacetylated chitin. This step was carried out by passing the sheet through a bath of acetic acid solution and then between squeeze rolls to remove excess solution and to force the solution into the sheet and to compress the sheet. The action of the acetic acid was stopped by placing the sheet on a drier at 100° C. two minutes after its application to the sheet. The effective concentration range of acetic acid solution and the high efficiency of the process when operated with the proper concentration of swelling agent are demonstrated by the following data:

Solution of swelling agent	Properties of sheets	
	Basis weight	Turpentine resistance
	25x38x500 ream	*Minutes*
Water at 50° C	43	6.
0.01% acetic acid soln. at 50° C	43	28.
0.05% acetic acid soln. at 50° C	43	1660.
0.10% acetic acid soln. at 50° C	43	Greater than 7000.
0.15% acetic acid soln. at 50° C	43	4950.
0.25% acetic acid soln. at 50° C	43	258.
0.50% acetic acid soln. at 50° C	43	11.
1.00% acetic acid soln. at 50° C	43	4.

The values given throughout for turpentine resistance represent for each value an average of 16 tests measuring the time required for turpentine to pass through the weakest spot of a 0.3 square inch test area of sheet at 50% R. H. and 25° C. using a bronze ring with 2 cc. turpentine colored with an oil soluble red dye. A control sheet formed from the same pulp under the same conditions of pressing and drying without addition of any film-former, had a turpentine resistance of 1.5 minutes. Another control sheet from the same pulp which had 3.2% deacetylated chitin added in the beater with no surface treatment by swelling agent, had a turpentine resistance of 4.0 minutes.

The effective concentration range of acetic acid solution for application to the sheet is between about 0.02% and 0.35%. Below 0.01% the acetic acid exerts very little swelling action, and above 0.35% concentration it swells the deacetylated chitin so rapidly that the optimum point is apt to be passed with the result that the imperviousness of the sheet may not be increased. Under the conditions present in Example I, an impervious sheet is produced when the concentration of the acetic acid is about 0.1%. In addition to being grease-proof, the sheet is quite water-resistant, and it possesses exceptionally high wet strength. The Mullen bursting strength of the sheet was 47, and this strength was decreased only 30% by soaking the sheet in water at 25° C. for one hour.

In the tests tabulated above, all factors except the concentration of acetic acid in the swelling agent were held constant. The result shows that the swelling reaction rate increases with the acid concentration and that under the conditions present the reaction rate with acetic acid of about 0.1% concentration is such that the optimum degree of swelling is reached in about two minutes. It is shown also that if the swelling action is terminated at this point the finished sheet is completely grease-proof as shown by the turpentine resistance test. If the swelling action is continued beyond this point, there is a rapid decrease in turpentine resistance.

In applying these results to the operation of a continuous paper machine of standard design, the optimum conditions to effect any desired result as to grease-proofness may be found by selecting the minimum acid concentration which will give the required result within the permissible time of treatment, having due regard to the dimensions and speed of the machine. Under the conditions of Example I, the operator would select acid of about 0.1% concentration if the maximum resistance is required. If the conditions are such that a longer time of treatment is permissible, the optimum resistance will be attained with a somewhat lower acid concentration but a longer time of treatment. If the requirement is for the optimum result in a shorter time, these tests show that this would be obtained by using an acid concentration above 0.1%. Where the requirement is for a moderate degree of grease-proofness, it is seen that this can be had within the time limit using an acid concentration of 0.05% or even less.

Deacetylated chitin has only recently been available to the art. In United States Patent No. 2,040,879 issued to George W. Rigby, there is disclosed a method for the preparation of a suitable grade of deacetylated chitin. In this method shrimp, lobster or crab shells freed from contaminating adherent material, are treated with 40% sodium hydroxide at 110° C. until the product is soluble in dilute acetic acid, after which the product is washed to neutrality.

A complete description of the construction of the tester used for measuring pulp freeness is given in U. S. Patent No. 1,857,100. The procedure used for measuring pulp freeness on this tester follows: Referring to the drawing in the patent of reference, the cup 18 is filled with water until it flows out the pipe 19 which fixes the water level in the cup even with the top of the screen 20. The stop-cock 19 is then closed and a dispersion of the pulp (1.0 gram bone dry weight of fiber and 999.0 grams of water at 25° C.) is poured into the glass tube 21. The stopper 22 is promptly removed and as the level of the pulp dispersion passes the 41 cm. mark 23, the stopwatch is started. As it passes the 31 cm. mark (that is, after a fall of 10 cm. from the 41 cm. mark) the watch is stopped. The elapsed time is the freeness of the pulp.

Example II

This example illustrates the fact that the swelling agent may be incorporated with the sized pulp just before sheet formation to give a grease-

resistant product providing the concentration of swelling agent is suitably adjusted to bring about a swelling reaction rate such that the film-former is swollen to the optimum degree in the time required to pass the sheet through the machine.

Pulp was sized with 1.6% deacetylated chitin by the method of Example I. The sized pulp was diluted to the desired consistency for sheet formation, and the portion of this required for a 43 pound basis weight sheet (25x38x500 ream) was used for sheet formation on a valley sheet mold. The portion was charged into the head box of the sheet mold, and acetic acid was added in an amount required to give the concentration stated below. After addition of the acetic acid, the pulp was stirred gently for eleven seconds and then the valve was released to allow the water to drain from the pulp and form the sheet. The time required for all free water to drain through the forming wire is recorded below as "Drainage time." The sheet was couched from the wire, pressed to 40% sheet dryness, and dried at 100° C. The following data illustrate the operation of the process:

Concentration of acetic acid in flow box	Drainage time	Turpentine resistance of sheet
	Seconds	*Minutes*
0.0000	11.5	1.5
0.0050	8.0	6.0
0.0075	9.5	28.0
0.0090	13.0	720.0
0.0100	15.0	720.0
0.0400	17.0	93.0
0.1000	17.0	33.0
0.4000	17.0	27.0

The action of the acetic acid was first to decrease the draining time, and then with increasing concentration the draining time increased to a maximum which held constant with higher concentrations of acetic acid.

In the above tabulation the time of exposure to the swelling action was held constant and the concentration of the acid was varied. The results show the marked effect of the acid concentration on the reaction rate. Under the conditions present this effect is seen to be such that when acting for the given unit of time the swelling rate corresponding to 0.01% acid brings the swelling action to the optimum point, as shown by the turpentine resistance. Beyond this concentration point the rate is such that there is over exposure and the turpentine resistance rapidly declines from the peak.

The conclusions to be drawn from Example II are in line with those to be drawn from Example I, namely that, for a given acid concentration, the time-swelling action-turpentine resistance curve rises with time of treatment to a point of maximum turpentine resistance and thereafter rapidly declines. In using this information in connection with a given problem, the paper maker will aim to adjust acid concentration within the permissible time limit so that the required degree of grease-proofness is obtained at a point on the rising portion rather than on the descending portion of this curve.

Example III

This illustrates the production of impervious paper in the primary paper making operation using as the film-forming material a cellulose derivative that is water-insoluble but which is dissolved by a cold sodium hydroxide solution of about 6% to 7% concentration and which remains dissolved in this concentration at room temperature.

The beaten pulp described under Example I was treated as follows:

	Grams
3.9 percent consistency pulp at 77 seconds freeness	4000
Water	3000
1 percent solution of low-substituted methyl cellulose in 6% NaOH	625
5 percent solution of sulfuric acid	900

The pH of the sized pulp was 5.1, and its freeness was 97 seconds. This gave a film-former content in the sheet of 4.0% based on dry weight of fibers.

The pulp was diluted to the desired consistency and a portion required to give a 43-pound basis weight sheet (25x38x500 ream) was used for each sheet. Sheets were formed, pressed to 40% dryness, and then treated with an agent which caused the gelatinous precipitate of low-substituted methyl cellulose to swell highly. This was done by passing the sheet through a solution of the swelling agent at 25° C. and then between squeeze rolls to remove excess solution from the surface. The action of the swelling agent was stopped by then passing the sheet through a 5% solution of sulfuric acid. This was followed by washing baths including first a water bath, then a 0.25% NH_4OH bath, and finally a water bath to bring the sheet nearly to neutrality. The sheet was then dried at 100° C. In the table that follows to illustrate the operation of the process, "Time of action" is the time allowed between the bath containing the solution of swelling agent and the setting bath of 5% sulfuric acid.

Composition of swelling agent solution		Time of action	Sheet dryness at application of swelling agent	Turpentine resistance
Methyl cellulose	Sodium hydroxide			
		Seconds	*Percent*	*Minutes*
None	None	10	40	2.
2.0%	6.0%	10	40	Greater than 7000.
2.0%	6.0%	30	40	Greater than 7000.
2.0%	6.0%	60	40	2200.
2.0%	6.0%	120	40	1200.
1.0%	6.0%	30	40	5300.
0.5%	6.0%	30	40	4800.
0.5%	7.0%	30	40	6000.

These results show that, with about 4% precipitated methyl cellulose and with a swelling agent consisting of methyl cellulose dissolved in caustic soda, complete grease-proofness may be attained providing over-exposure to the action of the swelling agent is avoided.

The sample of low-substituted methyl cellulose was prepared as follows: One thousand (1000) parts of sulfite cellulose were steeped in 10,000 parts of an aqueous solution containing 18% sodium hydroxide-13% sodium methyl sulfate. After standing for one hour at 25° C., the sheets were pressed to 3300 parts and placed in a close fitting, tightly sealed can which permitted no air to enter. The can with its contents was maintained at a temperature of 35° C. for four days, after which the sheets were removed, washed free from caustic in warm water, and dried.

A solution of the low-substituted methyl cellulose was made by dispersing 600 parts of the

above product in 10,000 parts of 6% sodium hydroxide solution and cooling to −6° C. with vigorous agitation. The solution was diluted to the desired concentration with sodium hydroxide solution at room temperature.

Example IV

This illustrates the use of a cellulose glycolic acid salt as a film-forming material. The beaten pulp described in Example I was used at a consistency of 1.9%. To this a sufficient amount of a 1.0% solution of sodium celulose glycolate (pH 6.8) was added to give the ratio of film-former indicated in the following table. After thorough mixing with the pulp enough alum solution was added to precipitate the sodium cellulose glycolate. After complete mixing, the pulp slurry was at a pH of 4.5. The slurry was reduced with water to a paper making consistency and sheets of 43-pound basis weight (25 x 38 x 500 ream) were formed. The control sheets were pressed and dried at 100° C. without any surface treatment with swelling agent. Additional control sheets were formed in the same way from the same pulp before the sodium cellulose glycolate and alum were added. The remainder of the sheets, after couching from the forming wire, were passed through a solution of swelling agent while supported by the couching felt. These were squeezed to 40% sheet dryness, and then they were dried at 100° C. The temperature of the swelling solution was 25° C.

These sheets that were given the swelling agent treatment, in addition to the high turpentine resistance, recorded herein, have a very high wet strength and translucency resembling parchment paper but the fiber identity is not destroyed.

Percent Na cell glycolate based on fiber weight in sheet	Swelling agent	Concentration of swelling agent	Turpentine resistance
		Percent	*Minutes*
None	None		0.5
1.0%	None		1.1
1.0%	NH_4OH	0.20	744.0
1.0%	NH_4OH	0.35	420.0
1.0%	NH_4OH	0.50	126.0
2.0%	None		2.0
2.0%	NH_4OH	0.10	7,500.0
2.0%	NH_4OH	0.20	7,500.0
2.0%	NH_4OH	0.35	7,900.0
2.0%	NH_4OH	0.50	10,000.0
2.0%	NaOH	0.10	8,200.0
2.0%	NaOH	0.05	7,500.0

The cellulose glycolic acid salts have a broader operating range of swelling agent concentration, especially that of ammonium hydroxide, than that of deacetylated chitin.

The concentration of sodium cellulose glycolate given herein is based upon the cellulose used to form the product which was made as follows:

One hundred twenty (120) parts of bleached sulfite pulp were steeped in 1200 parts of 25% sodium hydroxide for one hour, after which the sheets were pressed to 360 parts, mixed in a Monel metal Werner & Pfleiderer shredder for sixteen hours at 20° C. with 90 parts of dry sodium chloroacetate. To stop the reaction and viscosity reduction of the cellulose reduction of the cellulose derivative by oxygen in the air, the resulting unpurified product was mixed with sufficient water to give an 8% cellulose consistency. It was then diluted with 9490 parts of water and 1010 parts of 5% solution of sulfuric acid to give a 1% solution of sodium cellulose glycolate at pH 6.8.

Example V

This illustrates the operation of the process of this invention on a paper machine.

A beater was charged with a bleached sulfite pulp, and the charge beaten to a pulp freeness of 77 seconds. A 1.25% solution of deacetylated chitin in 0.375% acetic acid was added to the pulp in an amount equal to 3% by weight of deacetylated chitin based on the fiber, and after thorough mixing 1% ammonium hydroxide solution was added until the pH of the pulp was 9.4. The pulp was discharged into the machine chest, diluted to paper making consistency, and formed into a sheet on a cylinder paper machine (5" trim) operating at 10 feet per minute. From the forming wire the sheet passed between press rolls and was then passed through a bath containing a 1.25% solution of deacetylated chitin in 0.375% acetic acid, then between squeeze rolls to remove excess solution from the surface. When the sheet arrived at the first of the three driers, the film-former was in a highly swollen condition. The heat of the driers stopped the action of the swelling agent and dried the sheet. The elapsed time from point of applying the swelling agent to the point where the sheet contacted the first of the three heated driers was twenty seconds. The turpentine resistance of the paper was increased 1000 fold by this treatment with deacetylated chitin.

The example given below shows the effect obtained by using free pulps filled with commercial amounts of chalk to produce papers of the quality known as "book paper".

Example VI

To a beater furnish consisting of 60 parts bleached soda pulp, 15 parts bleached sulfite pulp and 60 parts calcium carbonate (all on air dry basis) was added 100 parts of a 1% solution of sodium cellulose glycolate at a pH of 6.8. When the sodium cellulose glycolate was mixed thoroughly with the beater furnish, 65 parts of a 3% solution of paper maker's alum was added. This mixture was diluted further with water to a consistency of 0.3%, it was formed into sheets on a hand mold and squeezed to 30% sheet dryness. These sheets were then treated with a 0.4% solution of ammonium hydroxide (swelling agent) pressed to 36% dryness and dried on a steam heated drier.

The dried sheets (50 lbs. basis weight for 25x38x500 ream) had a water resistance of 8 seconds, a turpentine resistance of 16 seconds, and Mullen bursting strength of 42 lbs. The chalk content of the sheets was 25%. Corresponding sheets with starch (5% based on added chalk) instead of the sodium cellulose glycolate had water resistance and turpentine resistance of less than one second each and a Mullen bursting strength of 38 lbs.

The film-former may be added to the fibrous ingredients and precipitated therein before admixture with the chalk or it may be added to both of the ingredients separately before they are mixed.

Example VII

This example illustrates the effect obtained by using pulps beaten to a freeness corresponding to bond paper pulps with a high hiding type of pigment. Under Example IV, following the addition of the 1.0% solution of sodium cellulose glycolate a sufficient amount of a 5% water dispersion of titanium dioxide was added to give 2%

titanium dioxide based on fibers. Example IV procedure was followed from this point of the process.

The sheets were opaque, white, of high wet strength and they had a turpentine resistance over 6000 minutes.

Other cellulose derivatives which are water-insoluble but soluble in about 6–7% sodium hydroxide after cooling may be substituted for the methyl cellulose under Example III. For example, low substituted glycol cellulose or viscose (cellulose xanthate) will substitute directly in this example and give equal results. Low substituted cellulose glycolic acid (soluble only in strong sodium hydroxide solution) may be used in the process although greater amounts are required to develop imperviousness.

The water-soluble salts of cellulose hydrogen phthalate, cellulose acid succinate, or cellulose acetate acid succinate may be substituted for the water-soluble salts of cellulose glycolic acid under Example IV. In the use of these equivalents, however, sulfuric acid is preferred in place of alum as the precipitant.

In general, the process of this invention may be practiced with any film-forming material which fulfills the requirements of the definition for a film-forming material given herein. The process whereby this film-forming material may be used for producing impervious paper in the primary paper making operation has been disclosed fully.

The process is not limited to the swelling agents used in the foregoing examples but any agent which has the proper swelling action on the film-forming material may be used in the operation of the process. For example, other acids such as hydrochloric acid, benzoic acid, propionic acid, citric acid, etc., may be used with deacetylated chitin, and potassium or lithium hydroxides may be used in place of sodium hydroxide in the case of the alkali-soluble cellulose derivatives. In the case of the cellulose derivatives soluble in strong sodium hydroxide solution, the concentration of sodium hydroxide required for swelling may be reduced appreciably by operating the bath of the sodium hydroxide solution at subnormal temperatures.

Numerous modifications of the process may be made without departing from the scope of this invention. For example, water-repellent substances such as wax emulsions or rosin size may be used in the process. A wax emulsion may be precipitated onto the fibers in the beater along with the film-forming material, or the sheet may be treated with a water emulsion of wax at an intermediate stage in the drying operation. Thus, a water-proof and quite moisture-proof as well as grease-proof sheet is produced. The opacity and brightness of the sheet may be increased by the addition of pigments, such as clay, chalk, lithopone, titanium dioxide, etc., or the sheet may be colored by the addition of suitable dyes. The pigment may be treated as a water slurry with the film-forming material before addition of the slurry to the pulp. Other surfacing treatments may be applied. For example, the sheet may be water-finished on the calenders and the water-finish may contain size and coloring materials.

The process may be operated with any paper making pulp of any freeness. For example, any kraft, sulfite, soda, cotton rag, or cotton linter pulp, or mixtures of pulps may be used. Other fibrous materials such as asbestos fibers may also be used, especially as a modifying ingredient of ordinary paper making pulps.

An important advantage of this invention is that it provides for the first time an operable process for rendering paper impervious through treatment with chemicals in the primary paper making operation. This chemical process makes it possible to use any paper pulp of any freeness for producing impervious paper. It makes possible the production of impervious paper of any thickness practicable of operation on paper machines. The products are not merely grease-resistant but completely grease-proof. The products are unique in that they are not only grease-proof, but they also possess high wet strength and water-proofness.

The product of this invention is particularly useful for wrapping and packaging foodstuffs. It may be used for the production of lubricating oil paper containers, and it finds general use where a paper is required that possesses grease and water resistance and high wet strength.

As many apparent and widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. In the manufacture of grease-proof paper by a process involving as a continuous operation the standard successive paper making operations of pulp stock preparation, sheet formation, pressing and drying, the new steps which comprise mixing paper pulp with size solution containing deacetylated chitin as the film-former, precipitating said film-former on the paper pulp, applying to the sized fibers within the primary paper making operation before drying the sheet formed from the sized fibers an aqueous solution of an acid swelling agent which swells the precipitated film-former without parchmentizing the fibers, allowing the swelling agent to react until the film-former is in a highly swollen condition, and before drying the sheet stopping the action of the swelling agent while the precipitated film-former is in a highly swollen state but before it has been dissolved to the sol state.

2. A process for making grease-proof paper which comprises mixing paper pulp with size solution containing deacetylated chitin as the film-former, precipitating said film-former on the paper pulp, forming the sized pulp into a sheet, applying to the sheet within the primary paper making operation before drying an aqueous solution of an acid swelling agent which swells the precipitated film-former without parchmentizing the fibers, allowing the swelling agent to react until the film-former is in a highly swollen condition, stopping the action of the swelling agent while the precipitated film-former is in a highly swollen state but before it has been dissolved to the sol state, and then drying the sheet.

LOUIS LEONARD LARSON.