June 6, 1933. F. H. McCORMICK ET AL 1,913,283

IMPREGNATED PAPER PRODUCT

Filed March 18, 1932 2 Sheets-Sheet 1

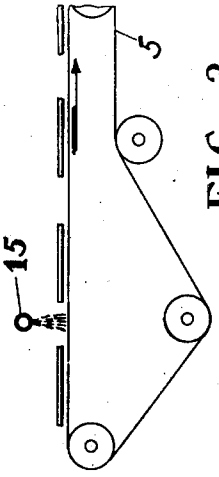


FIG. 3

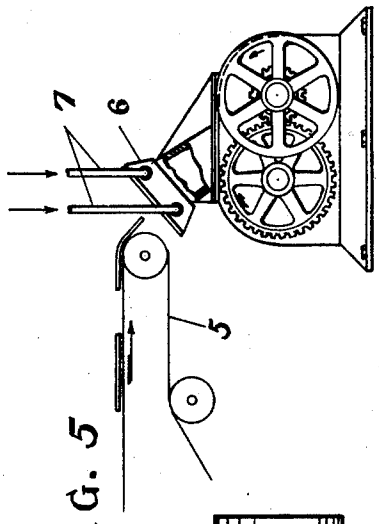
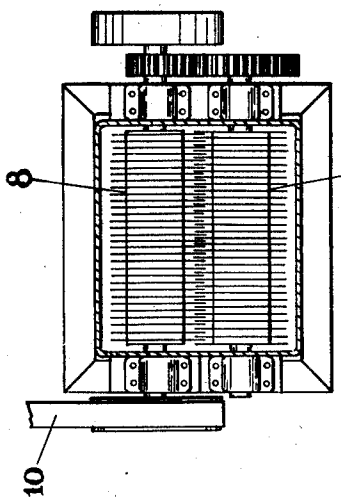


FIG. 4

FIG. 5



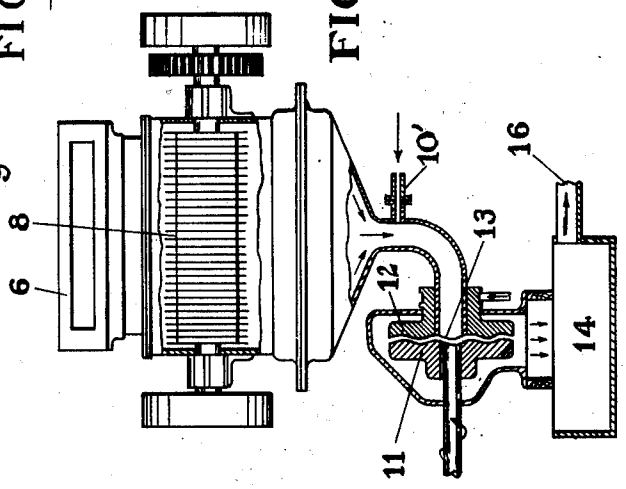


FIG. 2

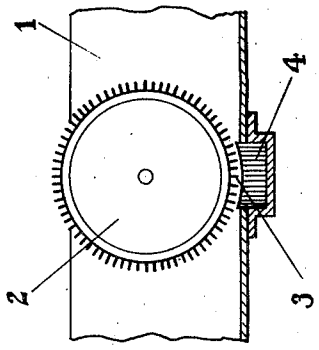


FIG. 1

Frank H. McCormick. Inventors
George L. Schwartz.

By Ralph F. Miller
Attorney

June 6, 1933. F. H. McCORMICK ET AL 1,913,283

IMPREGNATED PAPER PRODUCT

Filed March 18, 1932 2 Sheets-Sheet 2

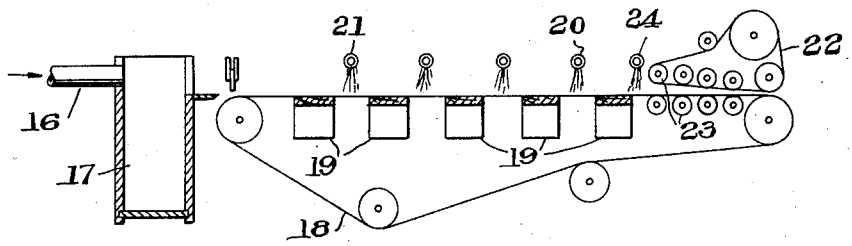


FIG. 6

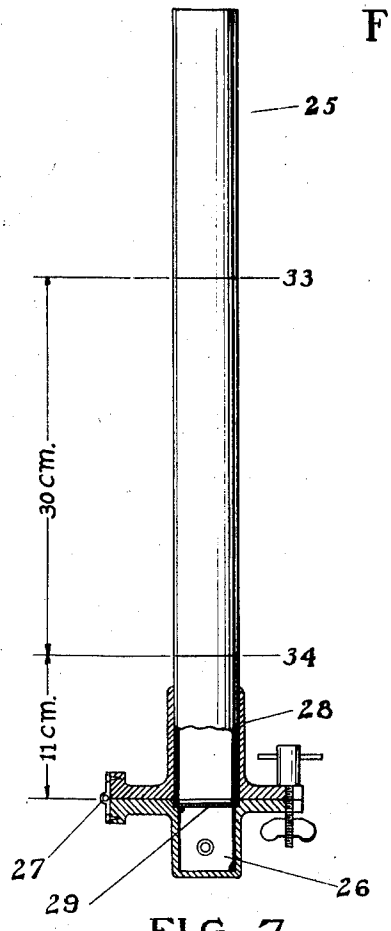


FIG. 7

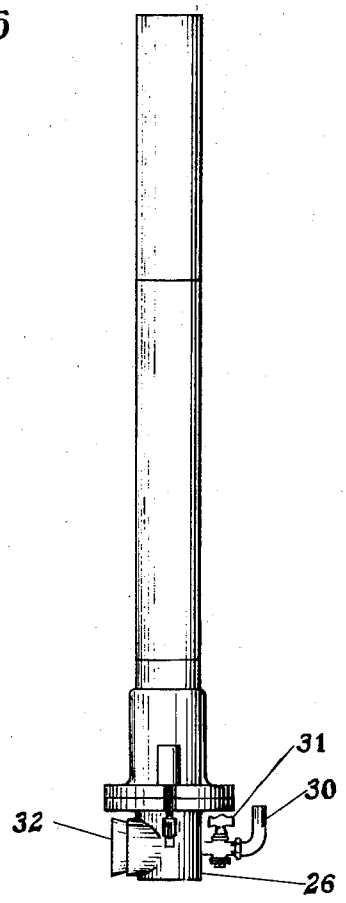


FIG. 8

Frank H. McCormick.
George L. Schwartz. Inventors

By Ralph F. Miller
Attorney

Patented June 6, 1933 1,913,283

UNITED STATES PATENT OFFICE

FRANK H. McCORMICK AND GEORGE L. SCHWARTZ, OF WILMINGTON, DELAWARE, ASSIGNORS TO E. I. DU PONT DE NEMOURS & COMPANY, OF WILMINGTON, DELAWARE, A CORPORATION OF DELAWARE

IMPREGNATED PAPER PRODUCT

Application filed March 18, 1932. Serial No. 599,808.

This invention relates to impregnated sheet material and more particularly to an impregnated cellulose fabric which exhibits to an exceptional degree those properties most desired in artificial leather products.

This case is a continuation in part of our Patent No. 1,857,100, which is continuation in part of our application, Serial No, 283,445, filed June 6, 1928. In these cases we have disclosed and claimed an absorbent paper or felt which is especially adapted for impregnation with colloidal impregnating materials exemplified by resins, pyroxylin and rubber.

Among the various methods suggested for making absorbent paper and impregnated products therefrom is one which consists of manufacturing a puffed paper by immersing a sheet of paper in strong caustic and drying the saturated sheet in air. The absorption of carbon dioxide causes the formation of sodium carbonate crystals which are subsequently washed out. The puffing effect is due to the formation of the crystals in the sheet. The long contact of the fibers with the strong caustic prevents any appreciable crinkling of the fibre. Furthermore, the restricted movement of the fibers when treated in sheet form prevents the formation of a base having the high degree of crinkle, high freeness and capability of uniform impregnation which characterizes the product of the present invention. Prior treatments of paper pulp with caustic have been chiefly concerned with the manufacture of high alpha cellulose through solution of the non-alpha cellulose by the caustic. The solution of the non-alpha cellulose bonding materials, which is the object of the process causes the original fiber to separate into the finer component fibers. The fibers are also shortened because the end portions, which are thinner than the middle portions, are dissolved off. This shortening and thinning of the fiber is evidenced by the slow freeness of the treated pulp and the decrease in the freeness value from that of the original pulp. High alpha cellulose papers now known are too expensive for general use as an impregnating base and the impregnated products possess certain deficiencies.

This invention has as an object the improved products resulting from the impregnation of the base disclosed in the above mentioned cases, and more particularly the improved products resulting from impregnation with colloidal impregnating materials which have a tendency to strain out on the surface of the usual paper or felts made for impregnation purposes. Another object is an improved method of making artificial leather and sheet impregnated products in general. Other objects will appear hereinafter.

These objects are accomplished by preparing a fabric base in the special manner disclosed in the mentioned cases and impregnating it with colloidal impregnating materials as will more fully appear in the following specification.

The fabric base is a paper or felt made of artificially crinkled cellulose fibers having a high freeness. The method of making the base, as disclosed in the mentioned cases, is briefly as follows: Paper pulp is treated with a solution of caustic soda of mercerizing activity under conditions which cause only a superficial reaction between the pulp and the caustic. To this end the reaction is stopped short of gelatinization, and the mercerizing action of the caustic is not allowed to proceed appreciably beyond a superficial or skin effect. The method of treating the pulp to bring about these conditions consists in dispersing the pulp with the caustic at high pulp consistencies (a low ratio of liquor to pulp) and diluting the caustic below mercerizing activity promptly after the fibers have been dispersed from the pulp mass and wet with the solution. By high pulp consistencies we mean consistencies above 10%, i. e., more than 10 parts by weight of pulp per 90 parts by weight of liquor. For most purposes, however, we prefer to use consistencies from 15 to 25%, while the maximum usable consistency corresponds to the minimum volume of liquor that will thoroughly wet the fibers in a time

short enough so that the concentration of the liquor is not materially lowered before all of the fibers are wet. Simultaneous with the wetting of the fibers with the mercerizing solution the crinkle and freeness of the pulp is at a maximum and these values decrease with increasing time of treatment. The use of high pulp consistencies have the effect of retarding the time action of the caustic on the fibers. Even with these high pulp consistencies, however, the solution should, for the best results, be removed promptly, a time as long as thirty minutes being usually undesirable except perhaps for certain highly resistant pulps such as rope. When using mechanism specially designed for swift dispersion of the fibers and prompt dilution of the caustic in contact therewith, it is not, except for economic reasons, essential that a low ratio of liquor to pulp be used.

The initial material is preferably kraft paper pulp. Unlike the process for treating pulp to make high alpha cellulose, the action of the caustic in the present process is stopped before any large amount of non-alpha cellulose constituents are removed from the fibers and before the fibers have been further divided into finer fibers by solution of the ligneous bonding materials and the non-alpha cellulose constituents.

Various other reagents may be used instead of caustic soda. These reagents are those which at suitable concentration and temperature are capable of dissolving or dispersing cellulose, the concentration of the reagent being within the range known as mercerizing strength, that is the concentration commonly used in mercerizing cotton goods. For a given concentration of these reagents the mercerizing activity of the solution is dependent upon the temperature. In the case of caustic soda, which is our preferred reagent, the activity increases as the temperature is lowered.

Inasmuch as the strength of a particular solution required to show a mercerizing effect may vary somewhat depending upon whether the fiber is more or less resistant than cotton fibers, we desire it to be understood that by solutions of mercerizing activity we mean solutions of such strengths which will produce the characteristic effects of mercerization in the particular fiber treated. The caustic content of a solution that may be designated as being of mercerizing activity at any given temperature is well understood by those skilled in the fiber art. A caustic solution of this strength improves the luster of fabrics and also improves the dyeing properties and tensile strength. The dye absorbency of the fibers of paper pulp is also increased, the X-ray pattern changed, the ease of hydration reduced, and the fiber changed from a flat ribbon form to a rod-like form.

The concentration of solution required to give the necessary mercerizing activity may, for practically all purposes, be defined as a solution having a mercerizing activity equivalent to that of an aqueous sodium hydroxide solution of 8% to 35% concentration at 25° C.

While the process may be operated between the freezing point of the caustic solution and the temperature at which degradation of the fibers begin (from −10° C. to about +104° C. for sodium hydroxide) it is ordinarily not desirable to operate at the lower and higher temperatures because the gelatinizing action at the lower temperatures and the degrading action at the higher temperatures takes place with such rapidity that it is difficult to effect distribution of the caustic throughout the pulp and to wash out the caustic to stop the reaction in time required to prevent the mentioned gelatinizing and degrading action from decreasing the amount of crinkle in the fibers below the desired value. It is preferred, therefore, to operate at temperatures not far removed from room temperatures. The best commercial operating conditions are between 20° C. and 40° C. with a concentration above 10%. We prefer to use an 18% concentration at room temperature.

The fibers must be in pulp form during the caustic treatment, and by pulp it is to be understood that we mean cellulosic fibrous material consisting of fibers not arranged into sheets and short enough and sufficiently low in diameter to be made into a uniform felt from a water suspension. The fibers must be of paper-making length, and long fibers, such as those separated from the raw materials by some form of degumming process, will not give the kind of product with which the present invention is concerned. Fibers that may be designated as paper making length have a minimum mean length of about ¾ mm. and a maximum mean length of about 4 mm. Because of the fact that fibers having a mean length of less than 1½ mm., such as the fibers of non-coniferous wood pulp, do not crinkle as intensely as the longer fibers within the paper-making range, we prefer, especially when working with the weaker solutions within the mercerizing range to use fibers having a mean length of 1½ to 4 mm.

The dry fibers may be added to an 18% solution, in sufficient amount to wet the pulp entirely, or the fibers may be added in wet form if the concentration of the solution is sufficiently higher to compensate for the water in the pulp. The mass should be agitated long enough to insure complete wetting, and excess caustic should then be removed by pressing or centrifuging. This

pulp is then put into a washer where is it freed from caustic solution or the last traces of caustic may be neutralized with acid. If kraft or sulfite pulp are used, the fibers are usually short enough to make into paper without further beating. If linters or rope or other long fibers are used, they will require some treatment in the beaters or Jordan, or both, before they can be made into paper. The pulps from these fibers are then made into porous paper using either a Fourdrinier or a cylinder machine. Various modifications of the standard machine may be used to conform to the peculiar "freeness" of the pulp but these vary with the kind of fiber used or the proportion of treated to untreated fibers used.

For a more complete understanding of the present invention reference may be had to the accompanying drawings in which

Fig. 1 illustrates a form of apparatus that may be used in carrying out the invention;

Fig. 2 is an elevational view partly in section of another mechanism for carrying out the invention;

Fig. 3 is a diagrammatical view of the conveyor for supplying the mechanism of Fig. 4 with pulp;

Fig. 4 is an elevational view of the upper portion of Fig. 2 showing arrangement of the hopper and conveyor;

Fig. 5 is a plan showing the arrangement of the toothed rollers in the mechanism of Fig. 4;

Fig. 6 shows the conveyor on which the treated pulp is washed or washed and felted;

Figs. 7 and 8 are elevational views of an apparatus for determining the freeness of the treated pulp.

An apparatus which may be used in carrying out the invention and which illustrates the required type of treatment for the distribution of the caustic throughout the pulp is the ordinary beater, referred to above and shown in Fig. 1, which consists of a receptacle 1 in which the power driven roll 2 may be raised so that the longitudinal bars 3 may clear the bed plate 4. The caustic solution and the air-dry pulp in a ratio to give a consistency above 10% is put into the beater with the roll raised slightly from the bed plate as shown in the drawings so that the bars 3 will squeeze the pulp against the bed plate and separate the individual fibers from the pulp mass and secure contact between the fibers and the caustic solution and cause wetting of the fibers in the shortest possible time without any abrasive or cutting action. Air-dry pulp, or pulp exposed to normal atmosphere, contains about 8 to 12% moisture.

A standard trade practice is to designate air-dry pulp as 90% bone dry or containing 10% moisture. The caustic concentrations are adjusted to compensate for the known amount of moisture in the pulp. The consistencies mentioned herein are upon the conventional basis of the ratio of bone dry weight of fiber to liquid. As soon as the mixing is sufficiently complete to insure wetting of substantially all the fibers a stream of water is run into the mixer to stop the reaction and the beater roll is run until the fibers are washed to neutralization. The reaction between the caustic and the fibers ceases immediately with the dilution of the caustic by the water. Since the desired reaction between the fibers and caustic is practically instantaneous and since beating or drastic treatment of the fibers during the mixing is undesirable it will be apparent that the best mode of practicing the invention involves mixing the solution with the pulp in an apparatus which squeezes the pulp without abrasive action and disperses it into the solution, and then diluting or washing out the caustic alkali to stop the reaction after a time not appreciably longer than required to completely disperse the fibers throughout the solution.

Example I

Kraft from southern pine dry weight	75 lbs.
Caustic soda 19.5% aqueous solution at 55° C	555 lbs.
Consistency	12%

The kraft pulp in sheets containing 60% water was added to the solution in the beater of 150 pounds capacity, and the roll was held about 3 mm. above the bed plate while the pulp was mixed with the solution. When the solution was distributed throughout the pulp, which required about 15 minutes, a stream of water was run into the beater to stop the reaction, the washing screen was lowered into the pulp and the beater was run until the pulp was practically free from caustic. This required three hours continuous beating and washing. The freeness of the treated pulp as determined by the described method was 27 seconds.

The washed fibers were then pumped into a mixing chest and thence through a Jordan where they were cut very slightly to shorten them in order to make the pulp run through the piping to the paper machine, and were then run into a molding chest where the fibers were formed into a sheet on a cylinder. The sheet of fibers was removed from the cylinder by a wet felt and carried through press rolls to remove excess water and thence over drying can until dry.

The prompt dispersion of the pulp into free fibers by the mercerizing agent and mechanical treatment is essential to give the fibers freedom to crinkle and to insure

treatment of each fiber with a solution of sufficient concentration to produce the desired degree of crinkle. Especially in high consistencies the selective absorption of sodium hydroxide from water by cellulose fibers is so great that treatment of pulp without prompt dispersion gives a spotty effect in which only part of the fibers are crinkled. If the dispersion is accomplished without abrasive action, none of the softened cuticle of the fiber is torn off and the weight loss is held at a minimum. The softening of the fiber cuticle will be held at a minimum and loss of valuable material prevented if the reagent is removed promptly as soon as the surfaces of all fibers are made wet with it.

Another form of apparatus for carrying out our process, which in some respects is better adapted for commercial practice, is shown in Figs. 2 to 6, inclusive. Air-dry pulp compressed into the usual commercial pulp board is fed onto a wire screen conveyor 5 where a shower 15 of sodium hydroxide solution of 18% concentration at room temperature falls upon them. The excess caustic solution which runs off the sheet is stored for further use by means not shown. Considerable of the caustic solution is absorbed by the sheets which causes them to swell and soften. These sheets promptly drop from the conveyor into the hopper 6 (Fig. 4) of a shredder shown in plan Fig. 5 and in elevation in Fig. 2. As the sheets enter the shredder they are showered with more caustic solution of 18% concentration from spray pipes 7. The rolls 8 and 9 are armed with teeth which overlap between the rollers and which tear sheets into pieces of about one-half inch in diameter. These rolls are driven by the belt 10 at different speeds, such as 100 R. P. M. and 600 R. P. M., respectively, by means of the smaller gear on the driven shaft of the roll 8 which meshes with the larger gear on the shaft of the roll 9. The pulp then drops down in a disc refiner where additional caustic is supplied through 10′ in such quantity as will bring the total amount up to a ratio of 4 parts solution to one part of pulp (20% consistency). As previously noted, the concentration of the solution may be made sufficiently higher than the final concentration desired in order to compensate for the water in the pulp. The pulp then passes to the center of the disc refiner constituted by the discs 11 and 12 where the fibers are dispersed from the mass and wet with the caustic without abrasive action on the fibers. The discs 11 and 12 have smooth interfitting corrugated faces as shown and are driven in opposite directions by a mechanism not illustrated at a relatively high speed and are set with a clearance of $\frac{1}{16}$ inch to $\frac{1}{8}$ of an inch so that each fiber is freed from the mass in the passage 13 which extends from the entrance at the center of the disc to the edges where they are thrown off by centrifugal force. From this disc refiner the pulp drops into a trough 14 where the reaction between the caustic and fibers is stopped by diluting the caustic which also lowers the stock density to a pumping consistency. The duration of the treatment, that is the time elapsing between the application of the caustic on the conveyor from pipe 15 and the deposition of the pulp into the diluted solution in the tank 14, is not more than 15 seconds. The pulp passes through the conduit 16 to the chamber 17 whence it passes over a wire screen 18 where it is formed into a thick sheet and washed free from excess caustic solution. While fresh water may be introduced into the trough 14 to wash out the caustic to stop the reaction, we prefer to use the caustic (below 6%) resulting from the counter-current washing system on the screen 18 so as to avoid dilution of the solution to the point where recovery of the caustic from the solution is no longer profitable. The numeral 19 designates a series of suction boxes between which the washing showers of water are directed. The shower 20 is water and the weak caustic washed through the sheet into the last suction box is pumped to the preceding shower forming a stronger solution in the suction box below. The concentration progressively increases until the solution in the second suction box resulting from the shower 21 contains about 5% caustic concentration which is pumped back into the tank 14. The solution from the first suction box, which precedes the shower 21 and which removes the excess weak caustic resulting from the treatment of the pulp in tank 14, is run into a concentrator for recovering the caustic by raising the concentration of the solution to the value required for conducting the process. After passing over the suction boxes the sheet passes under another wire screen 22 where it is pressed between two or more sets of squeeze rolls 23. If the treated pulp is not free from caustic solution before passing through the wires 18 and 22 a shower of diluted hydrochloric acid from the pipe 24 is sprayed onto the sheet ahead of the squeeze rolls. The squeezed pulp is now formed into wet laps which are ready to be charged into the beater for making into paper.

After the pulp is dispersed in the strong caustic solution and is diluted with water or dilute caustic solution, it should be washed free from caustic as soon as possible. Mechanical treatment in this stage is unnecessary but it is not so injurious as in the strong caustic stage. After the pulp has been freed from caustic solution, it may be stored indefinitely as wet laps or in dilute

pulp form or as dry pulp, and is ready for forming into sheets of felt at any time.

The paper-making stage of the process is carried on in regular paper making equipment with certain modifications indicated below. The consistency of the pulp in the beater is from 3% to 5%. For the preparation of the very absorbent material, only enough beating is done to disperse the fibers. The pulp is then dropped into chests where it is diluted with more water and it is then sent over a Fourdrinier machine at a consistency of 0.6 to 0.3%. Long agitation in the chests must be avoided to prevent formation of agglomerates. We also use a slow shake with an amplitude of at least three eights of an inch. The Fourdrinier wire has an up-hill pitch of at least one inch for six feet of length so the water can form a pool and so it will not rush over the wire fast enough to disturb the thin sheet of fibers that is formed as soon as the pulp reaches the wire. The pulp is so free that it does not hold water long enough to obtain a satisfactory sheet formation when the wire runs with the down-hill or horizontal pitch. We have also found it desirable to direct a shower of water on the sheet where the water is leaving the surface and draining through the sheet. The sheet then passes under a dandy roll over suction boxes, or suction roll, or both and then through the wet press. Metal top press rolls must be covered with felt to prevent the sheet from sticking. Rubber covered press rolls or stone press rolls require no felt covering. The sheet after leaving the wet press passes over regular paper machine dry cans. When it emerges from the drying system, it is run between calender rolls to soften the texture and is then made into rolls and cut with regular paper winding and slitting equipment. Sheets 0.100″ thick and above are cut into the desired lengths after leaving the wet presses and are dried in conveyor ovens without canvas felts. Sheets of maximum softness and bulk, especially those 0.100″ or above are made by omitting the wet press operation and are dried in conveyor ovens with subsequent pressing between calender rolls.

In the following examples the impregnating base was made from pulp treated with caustic in the mechanism shown in Figs. 2 to 6, inclusive.

Example II

Kraft pulp, 90% bone dry (freeness on special tester 45 seconds)	1,000 lbs.
Sodium hydroxide (aqueous solution 18.5% at 21° C.)	4,000 lbs.

The pulp was passed through the system with a fixed rate of feeding the solution and pulp so as to give a uniform consistency. The strength of the solution in contact with the fibers during the treatment was 18% and the time of treatment with this solution was 15 seconds. The freeness after completing the treatment was 21.2 seconds. The treated pulp gave a dark blue color with zinc chloriodine reagent.

A sheet of felt was formed from this pulp by the following process: The pulp was dispersed in Hollander beaters with the rolls in light brushing position for a half hour to disperse the fibers. The pulp was then let down into a preparation chest and after the pulp was diluted with some water and stirred just enough to keep it in suspension it was pumped into a Jordan in which the cone was backed off the bars to prevent cutting. Following dilution with more water in a machine chest the pulp was pumped to a flow box above plate screens where it was diluted to a consistency of 0.4%, screened and passed onto a Fourdrinier provided with three slices and having an up-hill pitch of one inch for six feet of length. The shake was thirty per minute at an amplitude of three eighths inch. The first press roll was felt covered. After drying on regular paper-machine driers the sheet was passed between two calender rolls to soften. The final sheet was .048–.050 inches thick and weighed 0.68 pounds for an area of 36 x 40 inches.

Example III

Kraft pulp, 90% bone dry (freeness on special tester 45 seconds)	1,000 lbs.
Sodium hydroxide (aqueous solution 10.75% at 21° C.)	4,000 lbs.

The pulp was passed through the system with a fixed rate of feeding the solution and pulp so as to give a uniform consistency. The strength of the solution in contact with the fibers during the treatment was 10.5% and the time of treatment with this solution was 15 seconds. The freeness after completing the treatment was 29 seconds. The treated pulp gave a medium blue color with zinc chloriodine reagent.

A sheet of felt was formed from this pulp by following the procedure given in Example II.

Example IV

Kraft pulp, 90% bone dry (freeness on special tester 45 seconds)	1,000 lbs.
Sodium hydroxide (aqueous solution 8.2% at 21° C.)	4,000 lbs.

The pulp was passed through the system with a fixed rate of feeding the solution and pulp so as to give a uniform consistency. The strength of the solution in contact with the fibers during the treatment was 8.0% and the time of treatment with this solution

was 15 seconds. The freeness after completing the treatment was 38 seconds. The treated pulp gave a light blue color with zinc chloriodine reagent.

A sheet of felt was formed from this pulp by following the procedure given in Example II.

In order to obtain the maximum increase in freeness and crinkle positive dispersing mechanism such as used in the examples should be provided to insure unrestricted movement of the fibers during the treatment. It is possible, however, to carry out the process by other methods in which the fibers are not too restricted mechanically against movement, and we desire it to be understood that by dispersing the fibers with the mercerizing solution, we refer generally to treatment under conditions which provide the requisite freedom of movement and uniform treatment of the individual fibers. For instance, the pulp may be treated in the form of a mat or sheet provided the individual fibers have sufficient freedom of movement and are not compacted or felted as in a finished sheet of paper. For example, a mat may be formed on a Fourdrinier or cylinder machine from untreated fibers from a water suspension or from a caustic soda dispersion below mercerizing activity and while the mat is still in a loose uncompacted condition, before heat drying, the caustic soda solution of mercerizing activity may be applied to the surface of the sheet. The force of gravity will carry the mercerizing solution through the sheet and all of the fibers will be crinkled "in situ", though not to the same degree as when they are dispersed in the form of pulp. Or when still further crinkling is required, the fibers treated in pulp form may be dried as loose pulp, or as loose sheets, and then redispersed to form sheets, thus adding still more bulk to the finishing sheet.

The caustic alkali may be replaced by solutions of other mercerizing reagents of equivalent activity as for instance solutions of zinc chloride, ferric chloride hexahydrate, cuprammonium, calcium thiocyanate, sulfuric acid, etc.

Among pulps other than kraft which may be used in the practice of the present invention are sulfite and soda pulp, bleached or unbleached. Pulps from sources other than wood may also be used by first subjecting the fibers to treatment which will reduce them to paper making length.

In order to obtain various degrees of absorbency and strength in the impregnating base, we may treat mixtures consisting of reactive fibers and fibers such as rope, which are less reactive to the treatment disclosed herein. Likewise, we may make the base material from various mixtures of the treated or crinkled fibers with untreated fibers. The treated fibers should preferably consist of 25% of the mixture.

The absolute freeness values referred to herein are the values obtained by using the special freeness tester shown in Figs. 7 and 8. The percent increase in freeness has been determined by the same instrument although it will be understood that this value is independent of the method of testing. The numeral 25 designates a glass tube $1\frac{13}{16}$ inches inside diameter having a metal cup 26 hinged at 27 to a base 28 on the tube which holds a wire screen 29 of 0.006 inches thickness and 50 x 70 mesh over the bottom of the tube. The cup 26 and base 28 have cooperating lugs opposite the hinge slotted to receive the threaded shank of a fastener extending from a head which rests on the lug extending from 28. The cup 26 is filled with water until it flows out of the pipe 30 which fixes the water level in the cup even with the top of the screen 29 so that the fibers of the pulp dispersed in the tube will not mat against the screen. The stop cock 31 is then closed and a dispersion of the pulp (5g. bone dry weight in enough water to make 1000 cc. at 25° C.) is then poured into the glass tube 25. The stopper 32, which closes an orifice $1\frac{1}{2}$ inches in diameter is promptly removed and as the level of the water of the pulp dispersion passes the 41 centimeter mark designated by the numeral 33, the stop watch is started. As it passes the 11 centimeter mark indicated by the numeral 34 the watch is stopped. The time elapsing in seconds for the water to drain through 30 cm. between the two points 33 and 34 is the freeness.

Pulp such as treated in accordance with the present invention with a solution at the minimum strength within the mercerizing range, about 8% caustic soda at room temperature, is increased in freeness about 14%. The percent increase in freeness becomes rapidly greater as the caustic concentration rises to about 18%. Above this concentration a very slight additional increase in freeness takes place until the concentration reaches about 24%, above which it is not desirable to go because the slight additional increase in crinkle does not justify the expense of higher caustic concentrations, and the wetting properties of the solution gets poorer, requiring at a 35% concentration a too large excess of the strong solution for complete wetting. The felts which give the most outstanding results in the process of impregnation with colloidal impregnating materials are those which have been made with pulps treated with mercerizing solutions equivalent to a sodium hydroxide solution above 10.5% at 25° C. which causes an increase in freeness of from 35% to as high as 60%.

The absolute freeness values of the pulps

used in the present process are unusually high and serve to identify the pulp. The absolute freeness may be as high as 15 seconds for a pulp having a freeness increase of 60%. In our process for producing improved impregnated fabric products the best results are obtained with pulps having a freeness between 15 and 28 seconds which corresponds to a freeness increase of 35% to 60% for pulps such as kraft pulp. Pulps of this freeness are obtainable by using caustic soda solutions of 10.5% to 18% concentration and above room temperature in accordance with Examples I, II, and III. Pulps having a final freeness of 28 to 40 seconds corresponding to a freeness increase of 15% to 35% are obtainable as indicated in the examples with 8% to 10.5% caustic soda at room temperature, also felt into products capable of absorbing large quantities of colloidal impregnating materials.

Our preferred method of impregnating the felt base with rubber, pyroxylin, resin and like compositions consists in passing the sheet from a roll through an impregnating tank containing these compositions as dispersions of 15% to 40% solids, at a speed regulated to give thorough impregnation. The impregnated sheet is first passed between two knives to scrape off excess dispersion and thence into a heated drying chamber. The dried product, on emerging from the chamber may be wound into a roll immediately, or it may be passed between embossing or calendering rolls to smooth the surface. When the impregnating material is an aqueous dispersion of rubber the sheet is preferably supported by screens and is passed between squeeze rolls for expression of excess latex composition. These squeeze rolls take the place of doctor knives that are used for impregnation with dispersions in organic solvents.

Example V

The felt of Example II was impregnated with natural rubber latex as follows: A sheet weighing 0.68 pounds for a 36 x 40″ area was impregnated with natural latex containing 36% rubber, (dry weight). Excess latex was squeezed out by passing the sheet between rolls. The sheet was dried by passage over paper drying cans equipped with a canvas felt. The dried product after conditioning at room temperature gave a rubber content of 48.9% had a Gurley densometer porosity of 3.6 sec.; a pliability of 7.7 units, an Elmendorf tear of 1680 g., and it showed no paper break when folded over a $\frac{3}{16}$″ mandrel.

Example VI

The felt of Example III was impregnated with natural latex to a rubber content of 48.1% by the same procedure as in Example V. Its Gurley densometer reading was 6.6 sec., its pliability was 13.6 units, its Elmendorf tear was 2100 g., and it showed no paper break when folded over a 6/16″ mandrel.

Example VII

The felt of Example IV was impregnated with natural latex to a rubber content of 47.3% by the same procedure as in Example V. Its Gurley densometer reading was 13.7 sec., its pliability was 23.0 units, its Elmendorf tear was 1350 g., and it showed no paper break when folded over a 14/16″ mandrel.

Example VIII

The felt of Example II was impregnated with the following pyroxylin dispersion:

	Parts
Pyroxylin	1.0
Bl. castor oil	2.0
Carbon black	0.5
Toluene	2.1
Ethyl acetate	1.4

Total solids absorbed was 36.0%. The Gurley densometer reading of the impregnated product was 0.30 seconds, its pliability was 9.8 units, its Elmendorf tear was 724 g., and it showed no paper break when folded over a $\frac{7}{16}$″ mandrel.

Example IX

The felt of Example III was impregnated to a solids content of 34.3% with the pyroxylin composition of Example VIII. The Gurley densometer reading of the impregnated product was 1.80 seconds, its pliability was 14.8 units, its Elmendorf tear was 791 g., and it showed no paper break when folded over a $\frac{7}{16}$″ mandrel.

Example X

The felt of Example II was impregnated with low viscosity rubber in gasoline as a 12.5% solution, the total solids absorbed, based on the weight of the impregnated material, being 28%. The impregnating mixture consisted of:

	Parts
Pale crepe rubber, well milled	75.0
Litharge	15.0
Sulphur	2.0
Accelerator	1.0
Pine tar oil	1.0
Whiting	6.0
Naptha	500.0

The Gurley densometer porosity of the impregnated product was 0.19 seconds, its pliability was 6.5 units, its Elmendorf tear was 950 g., and it showed no paper break when folded over a 2/16″ mandrel.

Example XI

The felt of Example I was impregnated with the following composition:

	Parts
Orange shellac	30.0
Gum storax	10.0
Ethyl alcohol	40.0
Ethyl acetate	10.0
Methyl alcohol	10.0

to the extent of 60% total solids based on the weight of the impregnated material. The dried product is useful for insulation purposes.

Example XII

The felt of Example II was impregnated with the following composition:

	Parts
Gum chicle (balata)	15.0
Gum Pontianak	15.0
Toluol	70.0
Total solids absorbed, based on weight of impregnated material	37%
Elmendorf tear, average	965 g.

This material is laminated by pressure and heat into material for belting, or soles for shoes.

Example XIII

A sheet felted from pulp made in accordance with Example II was impregnated with the following resin composition:

	Parts by weight
Glyceryl phthalate resin	65.0
Pigments	35.0
Drier	3.1
Naphtha (low boiling)	21.0

The paint penetrated practically through the sheet. The dried sheet contained 76.5% by weight of paint. The product is exceptionally tough, durable, flexible, strong, and has a high resistance to cracking when bent.

The resin in the above example was prepared by heating in an open kettle 17.11 parts by weight of glycerol, 27.09 parts by weight of phthalic anhydride, and 55.8 parts by weight of linseed oil acids. The temperature was brought up to 482° F. in one hour and held at that temperature for 3¼ hours. The batch was blown with carbon dioxide during the 3¼ hours at temperature. The resin has an acid number of 5±2.

The drier consisted of a 25% turpentine solution of lead and manganese linoleates in a ratio corresponding to 3 parts of lead to 1 part of manganese.

Example XIV

The felt of Example II was impregnated with the following asphalt composition:

	Parts
Blown asphalt (M. P. 180° C.)	50
Toluol	50

The Elmendorf tearing strength was 1450 grams and the solids absorption based on the weight of the product was 58%. Although the amount of asphalt absorbed in the sheet is unusually high the product was flexible and did not have an asphalt-like appearance.

The impregnated parts of the above examples are still relatively porous after impregnation, and coating films are therefore readily anchored to them. This makes possible the production of artificial leather of a highly pleasing appearance which is very limp and flexible and which at the same time is exceptionally strong.

The finishing coat for the impregnated products may be of the type known to be useful in the manufacture of artificial leather products. We usually prefer pigmented rubber and pyroxylin compositions such as the following.

Example XV

	Parts
Pyroxylin	1.00
Castor oil	1.90
Pigment	0.60
Ethyl alcohol (denatured)	5.00
Ethyl acetate	4.50
Butyl acetate	0.50

Example XVI

	Parts
Rubber (smoked sheet)	57.50
Zinc oxide	30.00
Litharge	8.50
Lamp black	3.00
Sulphur	0.75
Palm oil	0.25
Naphtha	200.00

Products impregnated with pyroxylin or resin compositions may be coated directly with pyroxylin compositions without the use of a sizing coat. The rubber impregnated products need no sizing coat for coating with resin or rubber finishes but a sizing coat is desirable for good anchorage if the finish is pyroxylin. A sizing coat of the following composition is suitable:

	Parts
Pyroxylin	4.00
Orange shellac	4.00
Ethyl alcohol (denatured)	25.00
Ethyl acetate	22.50
Butyl acetate	2.50

By the term "colloidal impregnating materials" as used herein we mean in general non-crystalline film forming materials which include not only true colloids such as resin and rubber, but also those impregnating materials which because of their high viscosity or because of other properties offer the same difficulties in the impregnation of ordinary absorbent papers which tend to strain out the pigments and large colloidal particles on the surface and prevent uniform impregnation of the interior

of the sheet. The following impregnating materials are representative of the class useful in the practice of our invention: cellulose esters and ethers; polymerizable substances such as ureaformaldehyde and chloro-2-butadien-1, 3 polymers; rubber in organic solvents or natural or synthetic aqueous dispersions; synthetic resins such as polyhydric alcohol-polybasic acid resins; natural resins such as rosin, damar, copal, and shellac; waxes such as paraffin, canauba, and ozokerite; greases such as petrolatum; drying oils such as blown linseed oil, blown China wood oil and blown fish oils; bituminous substances such as bitumens pyrobitumens, pyro-liquors, distillates, tars, and pyrogeneous residues from the manufacture of oils, fatty acids, fat, or waxes. Bitumens such as asphalts may be used in melted form, or in solution in organic solvents, or as aqueous emulsions. It will be understood that these materials for the greater part require the addition of certain modifying agents to make them useful for impregnation purposes. Thus, certain oils, and non-volatile esters are used with cellulose esters and ethers, blown vegetable oils with bituminous substances and natural or synthetic resins; tar with rubber, and resins with drying oils. Various pigments may be used to give color to the material.

Our improved artificial leather and impregnated products in general may be identified by separating the base from the impregnating and coating materials with suitable solvents and noting the freeness of the pulp of the base and its response to the test for mercerized fibers. If the pulp has been crinkled with caustic soda of mercerizing strength the fibers are not only changed as viewed through the microscope, from the ribbon-like to circular form, but they also respond to the test with zinc chloriodine which distinguishes pulps or papers treated with sodium hydroxide solutions of mercerizing activity. While pulps treated with this strength of caustic or periods longer than those which characterize the present invention also respond to the zinc chloriodine test, they are differentiated by their freeness, since they seldom have a freeness as determined by the method described herein faster than 60 seconds. Pulps that have been manufactured by the soda process in which wood chips are cooked with 8% to 11% of sodium hydroxide at high temperature and pressure show only a slight coloration easily distinguished from that obtained when this pulp is further treated with caustic as described herein.

The zinc chloriodine solution for carrying out the test should be prepared fresh for each test and may be made by adding 4 drops of a solution of 1 gram of iodine and 20 grams potassium iodide in 100 cc. of distilled water to 20 cc. of a solution of 280 grams zinc chloride dissolved in enough distilled water to make 300 cc. About 0.50 grams air-dry pulp is dispersed in a test tube with 100 cc. distilled water, the excess water drained off in a Gooch crucible and expressed by pressure to about 75% moisture. The pulp is transferred to a test tube containing 5 cc. of zinc chloriodine solution at a temperature of about 20° C. to 25° C. and shaken until dispersed. The prompt occurrence of blue color indicates that the pulp has been treated with about 8% to 35% sodium hydroxide. If the color is very deep, it indicates that the concentration of the solution (at room temperature) was above 13% and graduations of lighter shades indicate concentrations down to the point where mercerizing activity begins. Mixtures of treated and untreated fibers are recognized under the microscope after staining with zinc chloriodine solution. The color persists several days with bleached sulfite pulps treated by the present process. Unbleached kraft pulps treated likewise give a color almost black due to the brown color of the pulp and it fades within a few hours.

The advantage of using the felt or fabric herein disclosed in our process for making impregnated products will be apparent from the following table showing the values obtained by the kerosene absorption test which is a standard test for determining the volume of material capable of being absorbed by an absorbent paper. The first item in the table is the preferred base of the present invention made by treating pulp with 18% caustic soda as set forth in Example II. Item 2 is the base made from pulp treated with 10.5% caustic soda (Example III) which is about the lowest caustic strength that will produce a pulp within the preferred freeness range of 15 to 28 seconds. Item 3 in the table is the base made from 8% caustic soda which is just within the range of mercerizing activity. The initial freeness of the kraft pulp was 45 seconds in each case. The first three items in the table, therefore, show an increase in the freeness of 53%, 35.5% and 15.5%, respectively.

Base	Freeness seconds	Kerosene absorbed	Porosity seconds	Pliability	Paper break	Tear strength grams
1. Kraft 18% NaOH	21.2	364%	0.13	3.8	1 1/16"	80
2. Kraft 10.5% NaOH	29.0	306%	0.35	8.4	1"	175
3. Kraft 8% NaOH	38.0	212%	0.75	19.0	2"	242
4. Linters	34.0	169%	0.47	14.8	1 1/16"	264
5. Kraft 6% NaOH (2 hrs. at 100° C.)	46.1	158%	1.80	27.0	3"	260
6. Roofing felt	53.8	262%	0.35	5.5	1 1/16"	79
7. Alpha cellulose	75.0	155%	1.90	6.2	1 1/16"	190
8. Rag	201.0	115%	2.80	22.0	1 1/16"	412
9. Blotter	327.0	108%	0.20	17.3	1 3/16"	150

It will be seen from this table that the

percent kerosene absorbed decreases with the decreases in the freeness of the cellulose pulp from which the base is made. Roofing felt is made chiefly from animal fibers and is an exception.

In the following tables comparisons, as to residual or impregnated porosity, pliability, paper break and tearing strength, are made of the impregnated products of the examples and those resulting from similar impregnation of some of the best absorbent felts of the prior art which have been included in the preceding table. All the data in these tables are based on hand samples prepared under identical conditions. All samples impregnated with rubber latex contained 47% to 50% rubber based on final dried weight of the product except the base made from 6.1% caustic and blotting paper which would not take up more than 35% to 38% of rubber. The first three items of the column headed "Base" in each of the tables are the base materials made in accordance with the practice of the present invention and referred to in the preceding table, and the corresponding impregnated products are those of Examples V to X. All of the pyroxylin impregnated bases absorbed 34% to 35% solids except the blotting paper. The samples in the third table show the values obtained by impregnating with low viscosity rubber in gasoline as 12.5% solution. Blotting paper and linters partly strained out the solution.

The porosity values were obtained with the Gurley densometer, a standard machine in the paper industry. It measures the rate at which 100 cc. of air is passed through a circular disc of the material. The circular orifice has an area of 1 sq. inch. The pressure is obtained from a 20 oz. cylinder that fits into another cylinder. The lubricant is a low viscosity mineral oil. For the very porous products the readings are made on a 300 cc. air displacement but are calculated to 100 cc. for purposes of comparison. The figures for the tearing strength were obtained with the Elmendorf tear tester which is a standard testing equipment in the paper industry. The results are expressed as the sum total force in grams required to tear 16 individual sheets, eight with the machine direction and eight against. The sheets are 2½" square and are notched ½" with a knife at the point where the tear begins. The standard conditions are 50% relative humidity at 25° C. Comparisons as to resistance to paper break are made by stating the size of the smallest cylinder or mandrel around which the sheet may be rolled without the appearance of paper break. The pliability units were obtained by means of a special apparatus known as the Pfund pliability tester. The sheets from which the comparative data were obtained had a thickness of 0.045" to 0.050". If sheets of different thickness are used the values given for the impregnated products will vary accordingly. The impregnating base used in the practice of the present invention contains 0.68 pounds air-dry fiber for 36" x 40" area with a thickness of 0.045" to 0.050".

Latex impregnated

Base	Impregnation time seconds	Porosity	Pliability	Paper break cyl. diam. in.	Tearing strength grams
Kraft 18% NaOH	0.9	3.6	7.7	3/16	1680
Kraft 10.5% NaOH	1.4	6.6	13.6	6/16	2100
Kraft 8% NaOH	1.7	13.7	23.0	14/16	1350
Kraft 6.1% NaOH (2 hrs. at 100° C.)	2.9	20.0	38.0	1 1/16	1200
Alpha cellulose	1.7	24.4	10.0	4/16	2075
Rag	2.1	31.6	19.3	6/16	1200
Linters	1.7	20.8	11.5	10/16	975
Roofing felt	8.7	22.0	10.3	11/16	380
Blotter	11.0	48.9	14.2	4/16	230

Pyroxylin impregnated

Base	Impregnation time seconds	Porosity seconds	Pliability	Paper break cyl. diam. in.	Tearing strength grams
Kraft 18% NaOH	13.7	0.30	9.8	7/16	724
Kraft 10.5% NaOH	21.5	.60	14.8	7/16	791
Kraft 6.1% NaOH (2 hrs. at 100° C.)	38.0	1.30	19.2	15/16	760
Alpha cellulose	27.2	2.30	12.7	7/16	850
Rag	48.0	5.10	19.0	19/16	714
Roofing felt	16.7	.30	12.1	1/16	375
Blotter	136.8	8.90	25.0	7/16	226

Rubber (organic dispersion) impregnated

Base	Impregnation time seconds	Porosity seconds	Pliability	Paper break cyl. diam. in.	Tearing strength grams
Kraft 18% NaOH	24.3	0.19	6.5	3/16	950
Linters	96.0	.77	15.0	1/16	480
Roofing felt	59.0	.49	11.0	2/16	435
Blotter	600.0+	12.50	20.5	1 1/16	350

It will be seen from the above tables that the products of the present invention possess to a remarkable degree the properties most desired in artificial leather products. The residual porosity as measured by the time required for a given volume of air to pass through the impregnated sheet, is exceptionally high for the preferred products in which the base has been made from pulp treated with above 10.5% caustic. It should be noted that our product, item one in the table just above, absorbed 33.2% solids as compared to 22.2% for linters, 25.7% for roofing felt, and 14.3% for blotting paper.

The prior art materials which have sufficient residual porosity for the anchorage of top coatings are usually deficient in tearing strength. Known high alpha cellulose base material is not only too expensive for the purposes of the present invention, but

the impregnated products seldom possess satisfactory residual porosity except when the solids content is low and certain impregnating media are used. By means of the present invention, we obtain highly advantageous results without resorting to the usual processes of making highly purified pulp with attendant costs and further defibering into finer fibers. It is not intended, however, to exclude the use of a high alpha cellulose base in the practice of our invention because of the possibility of producing high alpha cellulose pulp of fiber length long enough to be increased to the requisite amount in freeness according to the process disclosed herein. While known high alpha cellulose pulp is increased in freeness by our process, the final absolute freeness is relatively low because the highest average length of high alpha cellulose fibers now produced is about 1.5 mm.

The advantages in our process for making impregnated products include the following: The felt has high porosity with sufficient strength to permit impregnation with concentrated dispersions of colloids or viscous liquids without breakage of the sheet or destruction of felt formation; the felt absorbs colloids consisting of particles too large for absorption by standard absorbent felts and the larger colloidal particles are not strained out in the surface of the sheet; the ratio of void size to fiber dimensions is greater than that of standard absorbent felts; the fibers are felted together like short wool fibers giving a heterogeneity of fiber directions that produce rapid penetration of saturants without undue surface spread; the fibers absorb (discharge) dyes more completely than untreated fibers; the treated pulp can be formed into such thick sheets that laminations are not necessary and these thick felts can be impregnated with very viscous liquids or with dispersions of relatively coarse particle size or with paints; the sheet has a high rate of wetting and penetration by colloid saturants which permits economic production of saturated products; the felt not only absorbs colloidal dispersions readily like wool but gives stronger impregnated products.

The capacity of the felt to absorb high concentrations of latices, colloidal dispersions, and viscous liquids makes it possible to express the excess saturant directly after absorption, which leaves the freshly impregnated sheet in a porous condition so evaporation will occur in the pores as well as from the surface. This method of drying prevents migration of the impregnating material to the surface, thus giving a final dried product with no accumulation of impregnating material on the surface. The accumulation of impregnating materials on the surfaces has always defeated efforts to make a leather-like product by impregnating other absorbent papers because the center core is softer and weaker than the surfaces which gives a laminated effect, which in turn increases the stiffness and emphasizes paper break. Our products, however, contain as much impregnating material in the central portion of the sheet as well as on the surfaces. Furthermore, the porosity is uniform throughout the entire thickness and the surfaces are not more saturated than the center portions with the result that the porosity of the sheet is greater than that of other absorbent felts. The surface porosity is essential to good coating properties and the resilience of the sheet makes it possible to apply heavy pressure when it is wet with saturant, without decreasing the thickness of the dried impregnated sheet markedly.

Our impregnated products have the saturant uniformly distributed throughout the sheet. This makes possible the production of extremely flexible products because the impregnating medium is not concentrated at the surface of the sheet due to the filtering effect of conventional absorbent papers on colloidal particles. The artificial leather products have the finishing coat firmly anchored because of the high residual porosity of the impregnated sheet. The product may contain large ratios of water resistant materials, such as asphalts, and yet retain felt-like characteristics.

Our products are useful not only as decorative limp artificial leather for book binding, etc., but are also particularly useful in shoe parts because the breathing properties (residual porosity) are comparable to leather. Our products are also useful for gasket materials, floor coverings, electrical insulation, wall coverings, and roofing materials.

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

We claim:

1. As an article of manufacture an impregnated sheet of felted artificially crinkled cellulose fibers, said fibers having a freeness of 15 to 40 seconds and having the substantially circular form in cross section which characterizes cellulose fibers treated with solutions of mercerizing activity.

2. As an article of manufacture an impregnated sheet of felted artificially crinkled cellulose fibers, said fibers having a freeness of 15 to 40 seconds and exhibiting a blue stain when treated with zinc chloriodide solution.

3. As an article of manufacture an impregnated sheet of felted artificially crinkled

cellulose fibers, said fibers having a freeness of 15 to 28 seconds and having the substantially circular form in cross section which characterizes cellulose fibers treated with solutions of mercerizing activity.

4. As an article of manufacture an impregnated sheet of felted artificially crinkled cellulose fibers, said fibers having a freeness of 15 to 28 seconds and exhibiting a blue stain when treated with zinc chloriodide solution.

5. As an article of manufacture a sheet of felted artificially crinkled cellulose fibers impregnated with colloidal impregnating material, said fibers having a freeness of 15 to 40 seconds and having substantially circular form in cross section which characterizes cellulose fibers treated with solutions of mercerizing activity.

6. As an article of manufacture a sheet of felted artificially crinkled cellulose fibers impregnated with colloidal impregnating material, said fibers having a freeness of 15 to 40 seconds and exhibiting a blue stain when treated with zinc chloriodide solution.

7. As an article of manufacture a sheet of felted artificially crinkled cellulose fibers impregnated with colloidal impregnating material, said fibers having a freeness of 15 to 28 seconds and having substantially circular form in cross section which characterizes cellulose fibers treated with solutions of mercerizing activity.

8. As an article of manufacture a sheet of felted artificially crinkled cellulose fibers impregnated with colloidal impregnating material, said fibers having a freeness of 15 to 28 seconds and exhibiting a blue stain when treated with zinc chloriodide solution.

9. Artificial leather consisting of strong, flexible, coated sheet material comprising a sheet of impregnated felted artificially crinkled cellulose fibers, said fibers having a freeness of 15 to 28 seconds and having the substantially circular form in cross section which characterizes cellulose fibers treated with solutions of mercerizing activity.

10. As an article of manufacture absorbent paper impregnated with colloidal impregnating material, said absorbent paper comprising a mixture of artificially crinkled superficially mercerized cellulose fibers and non-mercerized fibers.

11. The article set forth in claim 5 in which said impregnating material is rubber.

12. The article set forth in claim 6 in which said impregnating material is rubber.

13. The article set forth in claim 7 in which said impregnating material is rubber.

14. The article set forth in claim 8 in which said impregnating material is rubber.

15. The article set forth in claim 5 in which said impregnating material is a cellulose derivative selected from the class consisting of cellulose esters and cellulose ethers.

16. The article set forth in claim 5 in which said impregnating material is pyroxylin.

17. The article set forth in claim 6 in which said impregnating material is pyroxylin.

18. The article set forth in claim 7 in which said impregnating material is pyroxylin.

19. The article set forth in claim 8 in which said impregnating material is pyroxylin.

20. The article set forth in claim 5 in which said impregnating material is a resin.

21. The article set forth in claim 6 in which said impregnating material is a resin.

22. The article set forth in claim 7 in which said impregnating material is a resin.

23. The article set forth in claim 8 in which said impregnating material is a resin.

24. A process of manufacturing impregnated products which comprises dispersing paper pulp with a solution of mercerizing activity, stopping the reaction before it proceeds substantially beyond a superficial mercerization of the fibers, depositing a sheet of the crinkled fibers thus produced, and impregnating the sheet.

25. A process of manufacturing impregnated products which comprises dispersing paper pulp with a solution of mercerizing activity, stopping the reaction before it proceeds substantially beyond a superficial mercerization of the fibers, depositing a sheet of the crinkled fibers thus produced, and impregnating the sheet with colloidal impregnating material.

26. A process of manufacturing impregnated products which comprises dispersing paper pulp with a solution of mercerizing activity, stopping the reaction before it proceeds substantially beyond a superficial mercerization of the fibers, depositing a sheet of the crinkled fibers thus produced, saturating the sheet with colloidal impregnating material, and expressing the excess saturant directly after absorption.

27. The process set forth in claim 24 in which said solution has a mercerizing activity equivalent to that of an aqueous sodium hydroxide solution between 10.5% and 35% concentration.

28. The process set forth in claim 25 in which said solution has a mercerizing activity equivalent to that of an aqueous sodium hydroxide solution between 10.5% and 35% concentration.

29. The process set forth in claim 24 in which said solution has a mercerizing activity equivalent to that of an aqueous sodium hydroxide solution between 10.5% and 35% concentration, saturating the sheet with colloidal impregnating material, and ex-

pressing the excess saturant directly after absorption.

30. The process set forth in claim 25 in which the fibers of the paper pulp have a mean length greater than 1.5 mm.

In testimony whereof we affix our signatures.

FRANK H. McCORMICK.
GEORGE L. SCHWARTZ.