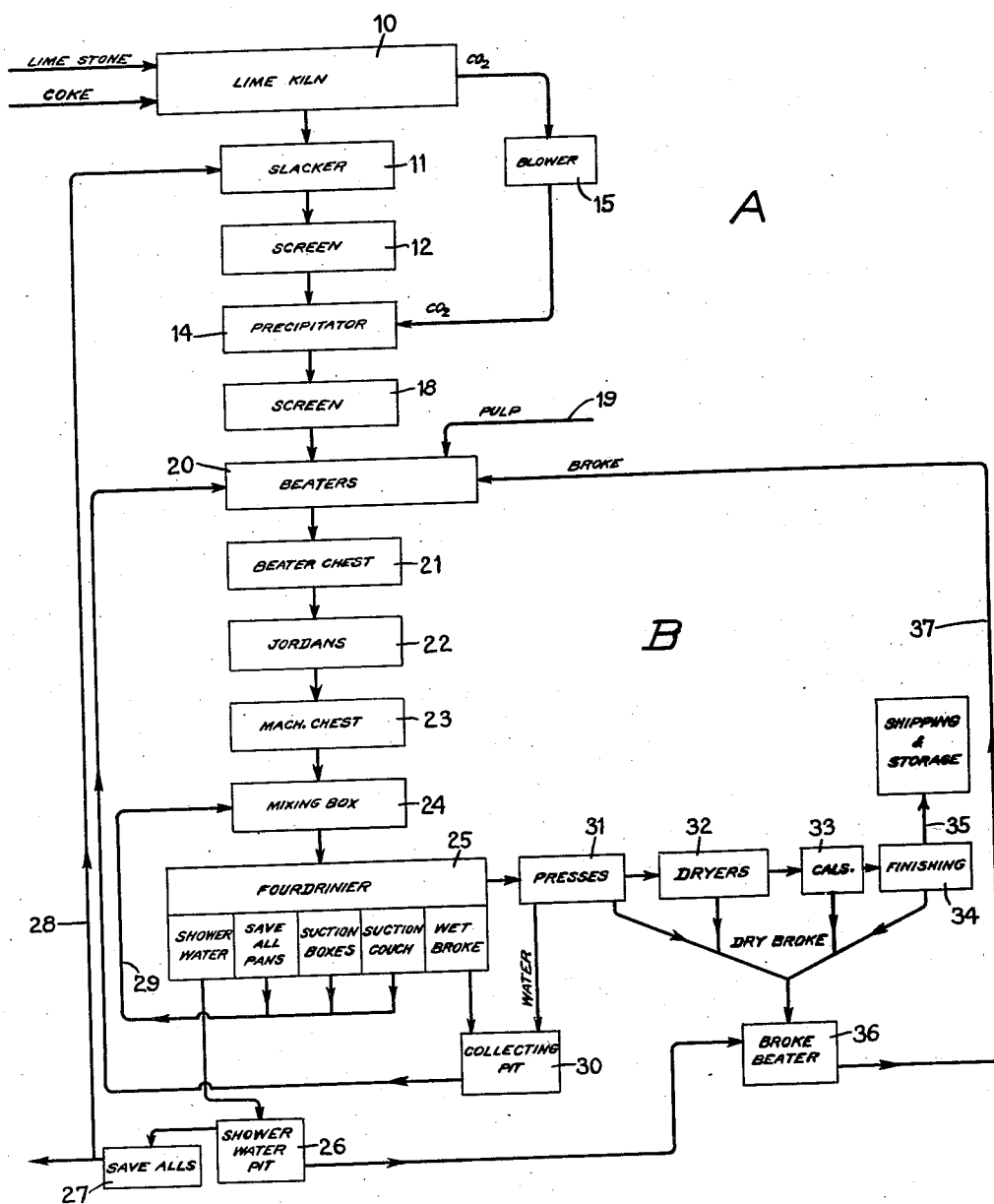


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PAPER AND PROCESS OF AND APPARATUS
FOR MAKING THE SAME

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This invention relates to an improved method of manufacturing paper and to an improved type of paper resulting from such method. More particularly it has to do with the production of a superior chalk-filled or coated paper, especially suited for printing or lithographic work. The product of the invention has a smooth, velvety finish which presents a better printing surface than any paper heretofore made. It has better color than prior papers and is more readily capable of absorbing the pigment carriers employed in inks. This results in quicker drying and enables the printer to shorten the time required for printing, while at the same time a clean, clear-cut impression of the type is obtained. A further feature of the improved product is its increased bulk in proportion to its weight and this advantage is obtained without decreasing the opacity of the paper. In fact the paper made in accordance with this invention has greater opacity than any papers of equal weight heretofore produced. Thus it may be stated that the improved process produces a paper having better printing qualities, better color, greater opacity and more bulk than papers of similar weight and character previously made.

While the improved process is particularly advantageous in the production of a printing paper having a smooth, glossy finish, it may also be used in the production of a high quality news print paper. In this connection the absorbent properties of the paper enable rapid printing without danger of smearing and the improved surface renders the product more desirable. The invention may also be utilized in connection with kraft papers and other paper products, in which case there results not only a better surface and better absorption properties for paints and inks, but a desirable filling is provided between the fibres. An advantage, particularly noticeable as the result of the better absorption, as applied to kraft paper or board as well as white paper, is the clear-cut or straight-line effect produced in any printed manner. The inks or coloring matter permeate the paper or board quickly, without spreading. The absence of off-setting is another advantage noticeable in the paper produced by the present method. Various other special products may be formed to advantage by the present invention. These may include, for example, highly absorbent paper toweling, shredded paper or pulp used in the manufacture of medical dressings, catamenial bandages, and the like.

A primary feature of the present invention is the addition to a paper pulp of freshly formed, precipitated chalk in suspension in the liquid in which it is produced. The chalk may be added to the pulp prior to its formation into the sheet, in which case it is thoroughly intermixed with the entire mass of pulp, or it may merely be applied to the surface of a sheet already formed in a paper machine, preferably on the wire side, if not on both sides, or it may be both mixed with the pulp and applied to the surface of the sheet.

Heretofore various pulverulent, substantially inert products have been added to pulp as a filler or as a coating or size in the production of paper for lithographic and printing purposes, other than newsprint paper. Powdered china clay has been used to a considerable extent for this purpose and precipitated chalk has also been used to advantage. The addition of these finely divided substances serves to fill the interstices between the cellulose fibres so that a smooth surface, suitable for printing, is obtained. Filling of the interstices in this manner also tends to increase the opacity of a sheet of given thickness. As heretofore employed the inert substance has been obtained in a dry, powdered state and has been first mixed with water to form a paste or liquid suspension and this has been added to the pulp mass or to other sizing ingredients to be added to the surface of the sheet. Now, we have discovered that greatly superior results may be obtained by the addition of a light precipitated chalk in the form in which it is originally produced and preferably when freshly produced. The addition of a given quantity of chalk in this form results in the production of a smoother and whiter finish, and gives to the paper a greater degree of opacity than can be produced even by the use of an equal amount of light precipitated chalk which has been dried and then mixed with water. There is apparently a greater uniformity of distribution of the chalk particles through the liquid as it is formed than can be obtained by mixing the dry powdered chalk with water. The colloidal character of the product as first formed is apparently more perfect and better suited to its use as a filler. This is made apparent by the greater viscosity of the material when originally produced than when dried and repulped. The dried chalk appears to be more crystalline and has a tendency to form coherent particles, thus increasing the size of the particles to be distributed through the pulp. There may be other explanations for the superiority of the chalk as formed over dry chalk repulped and we

do not intend to limit ourselves to any particular theory as to this.

The nature of the invention, and its other features and advantages, may be more readily understood by reference to the detailed description of an illustrative mode of carrying out the invention now to be given in conjunction with the drawing which illustrates diagrammatically a suitable arrangement of apparatus that may be employed.

The equipment required for the conduct of the process is suitable apparatus designated generally by the letter A, for the production of light precipitated chalk and a paper machine of any convenient form, designated generally by the letter B.

The equipment employed for the formation of the chalk may be of any convenient form and may be operated under any suitable conditions which will result in the production of a fine, light, precipitated product. Suitable apparatus for the purpose is disclosed in the patent to Statham, No. 1,266,339, granted May 14, 1918. It may comprise a lime kiln 10 adapted to receive successive charges of limestone and fuel, such as coke. In the consumption of the fuel it is converted largely into carbon dioxide and additional carbon dioxide is liberated from the limestone, thus reducing it to lime. As it is produced the lime may be withdrawn from the bottom of the kiln and passed to a suitable slaker or hydrator 11. Here a desired quantity of water will be added to produce milk of lime of suitable concentration. The milk of lime is then passed through a screen 12 for the elimination of suspended particles of undue size and the screened liquid is passed into a reaction vessel or precipitator 14.

The carbon dioxide which is developed in the lime kiln is also forced by means of a blower 15 into the top of the precipitator. By the means disclosed in my prior patent, the milk of lime may be sprayed or agitated, or both, within the precipitator to bring it into intimate contact with the carbon dioxide. The resulting reaction will bring about the precipitation of fine particles of chalk. The precipitator may be maintained during the reaction under substantially atmospheric pressure or, if desired, under a suitable super-atmospheric pressure of between, say, 20 and 100 pounds. The operating conditions may be suitably varied to fit the particular requirements. Preferably, the conditions will be so regulated as to bring about the production of as light and fine a chalk as possible. It will be understood that if desired the material undergoing reaction in the precipitator may be continuously circulated in the manner explained in the said Statham patent. Several precipitators may be employed in series, if desired.

When the carbonation of the milk of lime has been completed or carried to the desired point, the mixture of chalk and water is withdrawn from the precipitator and passed to a screen 18. The chalk slurry which passes through the screen may then be delivered directly to some convenient portion of the paper-making apparatus B where it will be thoroughly mixed with the pulp fibres. It will be understood that throughout the apparatus there will be provided suitable pumps, valves, and other handling and control devices, known in the art, for transferring the various materials from one point to another.

The paper-making equipment may be of any conventional form. Pulp which has been previously digested and washed may be introduced through a line 19 into beaters 20. The chalk slurry

may also be advantageously introduced into the beaters since they afford an excellent opportunity for thorough intermingling of the chalk and fibres. The stock used in the beater may include a certain amount of old stock, such as old magazines and the like, repulped. A suitable sizing mixture may be added to the material in the beaters. This may, for example, be a rosin size, in which case a dilute sulphuric acid solution will preferably be added at a later stage, as in the flow box to be described hereinafter, for the purpose of assisting in the setting of the size. The presence of the size, obtained from the old stock or separately introduced, seems to assist in the colloidal suspension of the chalk and therefore improves the distribution of the chalk through the fibres. Upon completion of the beating operation the mixture may be passed to a beater chest 21. This product may then be subjected to refinement in any suitable way, as by treatment in Jordans, indicated by the reference numeral 22. After refinement the pulp is passed to a machine chest 23. If desired the chalk slurry might be introduced at this point in lieu of going to the beaters. The mixture of the chalk and pulp, at the appropriate concentration for proper handling by a paper making machine, say between 1 and 2%, is then passed to the mixing box or flow-box 24 of such a machine. This portion of the equipment may be of any conventional form and need not be described in detail. As will be understood, the pulp delivered to the flow-box is spread over a wire screen or cloth forming an endless conveyor in a Fourdrinier portion 25 of the machine. Water which drains through the wire mesh is collected and utilized in various ways. The shower is preferably collected in a pit 25 and then passed to save-alls 27.

It will be found that the water accumulated in the save-alls 27 may be used to advantage in the slaking of the lime. For this purpose a portion of the save-all water may be passed through a line 28 to the slaker 11. In this way the chalk content of this water will be saved and other ingredients such as sizing substances, fine fibrous particles and the like, will assist in the formation of an excellent colloidal suspension. Excess water accumulated in the save-alls may be utilized in any convenient manner as in the washing of the pulp, and the like.

A portion of the water which is withdrawn from the pulp on the wire screen and collected in the save-all pans, suction boxes, suction couch, and the like, may be returned through a line 29 to the mixing box. Any wet broke which may be developed may be passed to a collecting pit 30 and after repulping may be returned to the beaters. The sheet of matted fibres formed on the screen may next be passed through sets of presser rollers 31 which serve to squeeze more of the water from the material. This water may be used to advantage in the pit 30 for the repulping of the wet broke.

In lieu of using a settling tank as a save-all, an automatic continuous filter may be used. This is made desirable by the presence of the fine chalk particles in the water. The chalk may be collected on the fibrous stock deposited on the filter surface. This solid matter may be repulped and added to the broke beater, later described. The water which passes through the filter may be used in part to slake the lime and in part to wash the pulp.

If desired a small quantity of lime may be added

to the white water removed from the pulp on the machine to bring about rapid settling of the filler and fibre. In this case it will be desirable to agitate the settled slurry with carbon dioxide gas to carbonate whatever free lime may be included in the slurry before returning this to the beaters or machine chest. The clear water from which the slurry has been removed should preferably also be brought into intimate contact with carbon dioxide in a suitable tower to carbonate the lime in solution prior to the use of this water for washing the pulp and the like. The carbon dioxide for this purpose may be obtained from the absorber or precipitator 14, since a considerable excess over that required at this point is developed in the kiln. Due to the reaction between alum and lime it will be undesirable to add lime in the manner indicated if any alum size should be present.

Upon leaving the presses 31 the partially dry web is passed between a series of drying rolls forming dryers 32 and then between calender rolls 33 and finishing rolls 34. The finished product, indicated by the arrow 35, may be passed to suitable winding equipment or may be taken care of in any other convenient manner for shipment or storage. Should the web of paper become torn in its passage through the machine, or upon leaving it, the portion which is destroyed may be passed to a broke beater 36 in which it is re-pulped, by utilizing some of the shower-pit water, for example, and then, through the line 37, it may be passed to the beaters 20.

It will be apparent that in addition to the improvement in the product resulting from the use of freshly formed wet chalk, certain benefits are derived from the fact that the chalk producing system and the paper making equipment are brought together and operated in a closed cycle. An economy is effected by the return of the waste products of one portion of the system to a point where the valuable ingredients may be recovered and utilized to advantage.

The quantity of chalk added to the pulp may be varied to suit the particular requirements. Beneficial results may be obtained from the addition of only small quantities. Generally it will be found advantageous to add sufficient chalk to form between 10 and 30% of the weight of the resulting paper. Due to the extreme fineness and even distribution of the wet chalk, however, even greater amounts may be used, if desired. At the same time a given quantity of chalk, added in accordance with this invention, will produce even better results than a chalk slurry formed from dry chalk. This may be illustrated by comparison of papers actually formed under substantially similar conditions from dry chalk re-pulped and from the wet chalk freshly formed. Paper produced by the use of dry chalk re-pulped was found to weigh 44.95 lbs. per ream, left an ash residue (CaO) of 15% and had an opacity of 73.2%. This is as measured by an opacimeter employing a photo-electric cell associated with a micro-ammeter; the paper tested is placed between a source of light and the cell and the degree of opacity is indicated on the ammeter. A similar grade of paper produced by the use of freshly formed wet chalk had a weight of 44.1, left an ash residue of 14.3% and had an opacity of 79.5%. Therefore, while the ash content indicates that there was actually less chalk in the wet chalk product, it had greater opacity. This would seem to show a more perfect, even distribution of the chalk particles when applied in the freshly formed, wet state. By way of comparison, it may be men-

tioned that a clay filled paper weighing 44.6 lbs. per ream and leaving 24.5% ash upon ignition, substantially equivalent to the chalk papers above mentioned, was found to have an opacity of 77.5%.

Another test which serves to indicate the difference between dried, precipitated chalk and the undried chalk is the following: 10 grams of dried chalk shaken into thorough suspension in 100 c. c. of water and allowed to stand for a period of 24 hours showed a bulk of 40 c. c. In one hour it had settled to 50 c. c. and in two hours it had settled to 45 c. c. A quantity of the wet chalk containing 10 grams of the solid particles, mixed with sufficient water to form 100 c. c. showed a bulk at the end of 24 hours of 60 c. c. It had settled only to 90 c. c. in one hour and 80 c. c. in two hours. The figures mentioned in each case represent the averages of three tests. This affords a further explanation for the superiority of the wet chalk product.

A further indication of the greater fineness and more even distribution of the undried particles is given by a viscosity test. It was found from a series of tests that 50 c. c. of a slurry of the undried chalk required an average of 73.5 seconds to empty from a standard 50 c. c. burette. Similar tests upon a slurry formed from dry chalk, having the same concentration, containing 8.9 grams per 50 c. c. of the liquid suspension, showed an average of 61 seconds required to empty the burette. The foregoing result is more startling when it is considered that in a grit and agglomeration test the undried chalk showed a great deal less residue than the dried chalk. One would naturally expect the agglomerated particles to interfere more with the discharge of the suspension from a burette but, in fact, the more even distribution of the wet chalk particles increased the viscosity of the liquid suspension to such an extent that a greater interference with the flow was produced. The residue in washing 56.2 c. c. of the wet chalk slurry through a 200 mesh screen was only .1% while a similar slurry containing 10 grams of dry chalk left a residue of .335% on a 200 mesh screen. In each case all but a trace of the residue was soluble in hydrochloric acid.

Various other tests have been conducted by way of comparison of the paper produced in accordance with the present improved process and paper having other fillers, such as dried chalk, clay and other known substances. These tests clearly show greater opacity resulting from the use of freshly formed, wet chalk than from the use of a like quantity of other fillers, such as clay and dried chalk. They further indicate that a product of greater bulk for a given weight is produced by the present process. That the improved paper is of lower density is demonstrated by the more rapid leakage of air through the paper when a pressure differential is maintained on the two sides. The advantage of the new paper with respect to rapid absorption and drying of ink during a printing operation is demonstrated by a penetration test. A mixture of 50% oil and 50% water is found to penetrate considerably more quickly through the improved, wet-chalk paper than through other filled papers of similar character. A marked improvement in the color of the paper resulting from the use of the present process may be noted. Paper containing the wet chalk filler is noticeably whiter than other papers produced from the same kind of stock and printing impressions on the new paper are clearer, sharper, and

otherwise improved. The improvement in the smoothness of the paper may also be readily observed.

While an illustrative form of apparatus and an illustrative method have been described in considerable detail, it will be understood that many variations may be made without departing from the spirit and scope of either phase of the invention. Other apparatus and methods for the production of precipitated chalk may be substituted for that disclosed. Furthermore, certain of the advantages of the invention may be obtained in connection with other forms of precipitated, finely divided fillers. For example, calcium sulphite may be produced instead of chalk by forcing sulfur dioxide, in lieu of carbon dioxide, into the precipitator and the precipitated sulphite may be introduced directly, while still in suspension, into the beater of the machine chest. Also, as previously indicated, the freshly precipitated chalk, or other substance, may be applied with other ingredients as a coating to either or both surfaces of a formed sheet, in lieu of clay or dried chalk, etc., in a manner well known in the art. It will be understood that the paper embodying the wet chalk filler may or may not be coated, as desired, and if coated the material used for this purpose may or may not include the same type of chalk. The disposition indicated for the various products of the different portions of the system is largely illustrative and may be varied to suit special conditions. The chalk may be mixed with the pulp fibres at points other than those indicated and the water withdrawn from the pulp at various stages may be otherwise utilized. The terms and expressions used herein are not to be regarded as terms of limitation but merely as suitably descriptive of the illustrative form of the invention.

What we claim is:

1. A method of making paper which comprises introducing into fibrous cellulosic material prior to formation therefrom of a completed sheet of

paper a substance comprising a salt of the group composed of calcium carbonate and calcium sulfite in its original suspension as freshly precipitated by a gas.

2. A method of making paper which comprises introducing into fibrous cellulosic material prior to formation therefrom of a completed sheet of paper a substance comprising chalk in its original suspension as freshly precipitated by carbon dioxide.

3. A method of making paper which comprises introducing into fibrous cellulosic material prior to formation therefrom of a completed sheet of paper a substance comprising calcium sulfite in its original suspension as freshly precipitated by sulfur dioxide.

4. A method of making paper which comprises forming fibrous cellulosic material into a continuous web, reacting slaked lime with a gaseous agent to produce a salt of the group composed of calcium carbonate and calcium sulfite, introducing the freshly precipitated salt into the cellulosic material prior to formation of the completed web of paper, draining water from the material as the web is being formed, and utilizing a portion of the water so drained in the slaking of the lime.

5. Paper comprising cellulosic fibres having incorporated between the same a freshly precipitated salt of the group composed of calcium carbonate and calcium sulfite deposited from its original suspension.

6. Paper comprising cellulose fibres having incorporated between the same freshly precipitated chalk deposited from its original suspension.

7. Paper comprising cellulose fibres having incorporated between the same freshly precipitated calcium sulfite deposited from its original suspension.

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