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PAPER MANUFACTURE

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20 Claims. (Cl. 92—21)

This invention relates to the manufacture of paper filled with alkaline filler.

This application is a division of my copending application Serial Number 584,012, filed December 30th, 1931, now matured into Patent No. 1,886,120, issued November 1, 1932.

The principal object of this invention is the manufacture of sized paper filled with alkaline filler.

An important object is the use as sizing agent of saponifiable material in substantially or preponderatingly unsaponified form.

A further object is the use of rosin in substantially or preponderatingly unsaponified form.

A further object is the employment of the principle of adding materials under conditions favoring the minimizing of the time and/or intimacy of contact of the constituents of the mix in connection with the sizing of paper filled with alkaline filler employing sizing material comprising saponifiable material in substantially or preponderatingly unsaponified form.

Other objects and advantages of this invention will become apparent during the course of the following description.

In numerous of my patents, for example No. 1,819,441, issued August 18, 1931, and Nos. 1,803,645, 1,803,648, 1,803,651, and 1,803,652, issued May 5, 1931, I have disclosed the sizing of paper filled with alkaline filler by the employment of a substantially unsaponifiable material such as paraffin in emulsified form. In other of my patents, for example, Nos. 1,803,643, and 1,803,647, issued May 5, 1931, I broadly cover the addition of alum or the like at the wet end of the paper machine, or in the beater and at the wet end of the paper machine, in the practice of the sizing, with any suitable size, of paper filled with an alkaline filler. Particularly I disclose therein the use as sizes of partially or completely saponifiable materials in saponified form, and preferably the use of size such as ordinary rosin size.

Rosin in papermaking is ordinarily employed in the form of rosin soap in which the rosin is wholly or partially saponified, in the latter case the saponified rosin holding the unsaponified rosin in emulsion form. In practice, the "free" rosin, i. e. the unsaponified rosin, even in such soaps as are known as "high free rosin" soaps, does not run much above 30 per cent of the total rosin present, and although it is perhaps considered theoretically feasible to make a usable soap with as high as 55 per cent free rosin, in practice 45 per cent may be said to be the upper limit. It will thus be noted that where rosin size is employed in alkaline filler paper mixes in the processes as disclosed in my prior Patents Nos. 1,803,643 and 1,803,647, a certain amount of rosin in unsaponified form may be present, which in the case of high free rosin soaps may amount to the theoretically possible 55 per cent of the total rosin present as explained above.

In the present application I disclose a process comprising the use of sizes comprising saponifiable material in substantially completely unsaponified or preponderatingly unsaponified form for sizing papers filled with alkaline filler. In its preferred practice the present process is a modification of the procedures covered broadly by the two patents last referred to. Saponifiable materials of any type whether partially or wholly saponifiable may be used in the present process. Examples are: fatty acids, esters particularly glyceryl esters of saturated and unsaturated acids, and esters of the high molecular fatty acids with alcohols, saponifiable gums, resins and the like, all whether chemically pure or occurring commercially in combination or association with other materials. In the class of saponifiable materials, however, I do not intend to include such black or substantially black colored materials of a pitchy nature which, because of their color, are not feasible for use in white papers, or even in papers which are somewhat colored such as kraft or the like.

I preferably use saponifiable materials which are solid or substantially solid at ordinary or room temperature and from the standpoint of cost I prefer to use rosin. In the present invention as stated I use either substantially all the saponifiable material such as rosin in unsaponified form; or, as in the case where saponified material as rosin is also additionally present in the furnish, I use the unsaponified material such as rosin in a substantially preponderating amount over that of the rosin present in saponified form, which differentiates from my prior disclosure.

The advantage of using saponifiable material in completely or preponderatingly unsaponified form rather than in saponified form is that in certain cases there is less tendency to foam formation. This is particularly useful in the case where coated broke is employed in the furnish. Also there is less tendency in certain cases for the web to stick to the press rolls or the like on the paper machine. Moreover in certain cases it is possible to effect an economy in the amount of sizing material employed as well as in the amount of alum used. There is also a tendency

for the sizing to be less affected by the deteriorating influence of alkaline filler.

Moreover the use as a size of saponifiable material such as rosin in completely or preponderatingly unsaponified form has an advantage over the use of paraffin, which is a substantially unsaponifiable material, because paraffin, although advantageous from the standpoint of increasing the flexibility of the sheet, has a tendency to weaken the sheet in respect to certain of its strength tests, such as the bursting or Mullen test. This disadvantage rosin does not have, rosin in fact exerting substantially no deleterious effect on the strength of the sheet.

As has been fully described in my two prior patents last referred to, when an acidic agent such as alum is utilized with a size in a relatively concentrated fibrous mix in the presence of an alkaline filler, there takes place a deterioration or destruction of the sizing by alkaline filler. This is avoided if materials are added to the mix according to the "minimizing principle". The phenomena on which this principle is based have been described by me in great detail in these two patents last referred to as well as in numerous other of my issued patents.

Briefly the situation is that alkaline filler, which always is present in the stock from which paper filled with alkaline filler is made in great stoichiometrical excess over the acidic constituent, acts upon the acidic constituent to the ultimate destruction thereof and/or the destruction of the effect maintained by such constituent. (The acidic constituent so-called may be one which is actively acid, and/or one, such as a size precipitate, which is capable of being affected or deteriorated by an alkaline material). The action just referred to has been found to depend upon the time of contact of the acidic and alkaline constituents and also upon the intimacy of contact of these constituents. Agitation such as normally occurs in papermaking procedure in stuff chests or the like accelerates the rate of reaction, but agitation at low concentrations while having some effect is not nearly so deleterious. Based on these observed phenomena a practical application has been developed whereby, by utilizing the "minimizing principle", i. e. by minimizing the time and/or intimacy of contact of the acidic and alkaline constituents, the acidic constituent and/or the effect produced thereby is substantially preserved in an alkaline filler mix. With the present types of paper machines and the present arrangement of equipment usually employed in paper machine operation, the contact of the acidic material and the alkaline constituent at any time prior to the passage of the stock from the last stuff chest, which is commonly called the "machine chest", results in great deterioration or complete destruction of the acidic material. Addition of one or both of these constituents, as well as other materials such as size, sodium silicate, starch, or the like, as set forth in my various issued patents, at a point subsequent to the passage of the stock from the machine chest, after which point according to present day operating practice the stock remains in concentrated condition only for a very brief interval of time, or addition preferably at or subsequent to the point of dilution, i. e. at the wet end of the paper machine, serves to substantially conserve the acidic material and/or effect thereof in the fibrous mix. It is this so-called "minimizing principle" which I prefer to utilize in the practice of my invention. It is obvious that the above description of the minimizing principle is merely a condensation of the full discussion given in a number of my prior patents, and indicates the practice by which the optimum results may be obtained. It is to be understood, of course, that minimizing of the time may be practiced,—without so completely satisfactory results to be sure,—by addition of material late in the process, but earlier than under the optimum conditions, such as in the chest or the like, see my patents Re. 18,983, 1,803,642, etc.

In the preferred practice of my invention, there is prepared in any suitable container such as a beater, a fibrous mix of any desired fibrous constituents, to which is added alkaline filler, and size for example rosin in substantially or preponderatingly unsaponified form, preferably as an aqueous emulsion. A precipitant such as an acidic material, preferably alum, may then be added. A variation which is sometimes desirable to practice is to add the size and alum to the fibre prior to the addition of the alkaline filler. After any further desired treatment of the mix such as is customary to prepare it for use, is then diluted preparatory to running off on the web-forming device. Preferably at this point a further amount of acidic material as alum may be added; or the original addition of alum may be omitted if desired and alum added only at the dilute stage. In the first instance the alum added at the dilute stage acts as a restoring agent, in the second as the original precipitating or fixing agent. Various other orders of addition of materials may be used in accordance with the minimizing principle as has been set forth in my various patents or copending applications. For example, the alkaline filler, alum, and/or size may be added at the dilute stage, as well as other constituents of the mix. The mix is then run over a web-forming device and through the remainder of the customary equipment of a paper machine, such as driers, and calenders, if desired, producing thereby a satisfactorily sized paper filled with alkaline filler. The paper produced by my process is thus what is known in the art as sized filled paper and by mere observation cannot be readily distinguished from ordinary clay filled paper sized with ordinary rosin size. However, apart from the effect on the paper of any other constituent which may be present in the size I employ, casein, as is well known, imparts to paper in which it is employed among other qualities, the quality of stiffness, strength or the like. Thus where in the claims I use the term "size", as referring to "casein-containing size" or "size" in the composition of which casein is included, or the word "casein" itself, such words are used as meaning material which may impart to paper in some degree, or material which may have imparted in some degree to the paper in which it is present among other qualities the quality of stiffness, strength or the like.

Emulsions for use in my process, such for example as those to be described below, may in certain cases be used directly with the alkaline filler in the fibrous mixture and run off on a web-forming device without the addition of alum according to the minimizing principle. In such case however, the emulsions are not fixed on the fibre, and thus much of the emulsion is lost in the white water, substantially the only amount remaining in the sheet being that which is mechanically retained by the web. When alum is employed as in the preferred practice of my invention outlined above, this suffices to fix certain

of the emulsions very satisfactorily on the fibre, and others of them with a fair degree of satisfaction. However it is sometimes desirable to employ instead of alum, or additionally therewith, fixing agents such as two mutually precipitating or flocculating materials. As alum itself is an excellent material for use as one of the mutually flocculating agents, it is sometimes convenient to employ with alum only one other material which with alum will form a flocculate or precipitate. Examples of mutually flocculating materials which may be employed are: soluble salts such as sodium silicate and acidic material as hydrochloric acid; barium chloride and sodium sulphate; and the like. Examples of materials which flocculate with alum are sodium hydroxide, sodium silicate, soap such as rosin soap; and the like. These may be added in the beater and/or dilute stage, but it is desirable that when the precipitation or flocculation takes place the emulsion I employ should be already present in the mix.

It is to be understood that my invention may be practiced without employing the minimizing principle. Thus the emulsion may be added with the fibre and alkaline filler in the concentrated stage of the paper making operation as in the beater, without alum as described above, or in the beater with alum and with or without other flocculating materials. While in certain cases moderately satisfactory results can thus be obtained, I prefer however to employ the minimizing principle as superior results are usually obtained thereby.

In order that rosin in substantially or preponderatingly unsaponified form, such as I employ in the practice of my invention, may be used in a fibrous mix, it is necessary that the rosin be introduced in extremely finely divided condition, preferably as a finely divided suspension or emulsion. Such suspensions or emulsions of rosin may be prepared in a number of ways.

For example, rosin may be thus emulsified by mechanical dispersion with a small percentage, for example about 2 per cent of a protective colloid such as alkali casein according to the so-called "Bewoid" process to form the so-called "Bewoid" size, (see Canadian Patent No. 305,650 of November 11, 1930). When alkali casein is used for emulsifying rosin according to the Bewoid process an amount of alkali is usually employed with the casein which is somewhat more that that required to completely dissolve the casein. Thus a certain amount of unacted upon alkali comes in contact with the rosin which may result in the conversion of a small amount of the rosin into soap form. However this may be, it is within the bounds of reasonable commercial accuracy to state that the rosin in Bewoid size is present substantially completely in unsaponified form.

Another suitable method is to emulsify rosin with a substantially insoluble type emulsifying agent, for example such method as is described for paraffin in my issued Patents Nos. 1,803,651 and 1,803,652. This may be done by melting rosin and vigorously mixing the melted rosin with a paste formed of emulsifying material and a liquid such as water, whereby the rosin becomes the disperse phase of the emulsion, the particles of rosin being substantially surrounded by the substantially insoluble emulsifying agent. Various emulsifying agents may be used, such for example as clay, more advantageously colloidal clay such as bentonite. A modification of this method is where the substantially insoluble emulsifying agent is formed by precipitation in the presence of finely dispersed particles of molten rosin in liquid suspension.

Still another suitable way in which rosin may be emulsified is by making a substantially non-breakable emulsion therewith such for example as is described for paraffin in my issued patents, Nos. 1,803,645 and 1,803,648. In this case the melted rosin is emulsified with a solution of a gum preferably substantially water soluble such as gum ghatti and other additive agents may be employed such as dextrin. One such emulsion may be made by the use (by weight) of 15 parts of rosin, 1 part gum ghatti, and 1 part dextrin, suitably with 83 parts water to give it a convenient concentration. The emulsion may be made in a colloid mill or homogenizer. Owing to the fact that rosin below the boiling point of water is very viscous and thus comparatively difficult to emulsify, it is preferable to employ temperatures higher than 100° C. for its emulsification, that is, the system should conveniently be kept under pressure in order to keep the water used in liquid condition at the elevated temperature desirable to employ.

In order to overcome the desirability of using such high temperatures as will make the rosin very fluid, it is sometimes feasible to utilize other materials which will lower the melting point or increase the fluidity of the rosin melt when in admixture therewith. These constituents may be used in any desired amount but owing to cost considerations, it is generally desirable to use only a minor amount, and such a minor amount is normally all that is necessary, 5 to 25 per cent usually sufficing. Suitable materials to use in conjunction with the rosin are paraffin, rosin oil, petrolatum, or any other liquids, oils or fluxible olids which will lower the melting point or decrease the viscosity of the rosin melt.

Other methods of preparing suitable emulsions are possible but these examples will suffice.

An example of a furnish suitable for carrying out my invention is as follows:

Added in the beater

	Pounds
Fibrous furnish, e. g. sulphite pulp, soda pulp and old paper stock	1000
Alkaline filler, e. g. calcium carbonate magnesium hydroxide	200
Emulsion of saponifiable material in substantially unsaponified form, e. g. rosin, (based on weight of rosin)	20

Added continuously and proportionately at dilute stage of the papermaking process

	Pounds
Acidic material, e. g. alum	25

Another example is:

Added in the beater

	Pounds
Sulphite and soda pulps	700
Coated broke (containing about 70% fibre)	430
Alkaline filler, e. g. calcium carbonate magnesium hydroxide	100
Emulsion of saponifiable material in substantially unsaponified form, e. g. rosin (based on weight of rosin)	17.5
Rosin size (based on weight of rosin)	2.5
Acidic material, e. g. alum	10

Added continuously and proportionately at dilute stage

	Pounds
Acidic material, e. g. alum	20

Another example is:

Added in the beater

	Pounds
Sulphite and soda pulps	700
Coated broke (containing about 70% fibre)	430
Bewoid size (based on weight of rosin present)	20
Acidic material, e. g. hydrochloric acid	2
Alkaline filler, e. g. calcium carbonate	100

Added continuously and proportionately at dilute stage

	Pounds
Acidic material, e. g. alum	20

It is to be understood of course that these furnishes are to be taken only as illustrative examples of my invention, and that they are in no way limiting, as it is possible to vary these formulae widely both as to ingredients and proportions and order of addition, and still obtain satisfactory results.

Instead of, or in addition to, introducing my emulsion into the fibrous mix, I may apply it to the web, by which is intended to be included the web either during the process of its formation or after it has been formed. This application to the web may take place either on the paper machine or subsequently. If desired, a precipitant or mutually flocculating precipitants may be applied to the emulsion prior to its application to the web, or a precipitant or mutually flocculating precipitants may be applied to the web at the same time as the emulsion, or independently thereof. Any known method of making such application is suitable.

Where I use the word "rosin", I intend to include not only the natural resin, but any synthetic resin acid or acids.

In place of alum I may use other aluminum salts or other metallic salts such as zinc sulphate or the like, or other acidic materials such as acid, sodium bisulphate or the like.

By the term "alkaline filler' I mean substantially water insoluble filler which when agitated in contact with freshly boiled distilled water, say for an hour, will impart a pH value to such water greater than 7.0, that is, which will be on the alkaline side of the neutral point. Among fillers included in this group may be mentioned calcium carbonate, of which lime mud from the causticizing process is one form; calcium carbonate magnesium basic carbonate employed in the paper disclosed in my United States Patent No. 1,595,416 issued August 10, 1926; calcium carbonate magnesium hydroxide disclosed in my United States Patent No. 1,415,391, issued May 9, 1922; and other substantially water insoluble normal or basic carbonates of alkaline earth metals (which expression is herein intended to include magnesium), or compounds, double salts, or physically associated mixtures of these with one or more other acid soluble materials of a substantially water insoluble nature.

By the term "alkaline filler", I also intend to include fibrous material and/or other material such as paper coating constituents or the like containing one or more compounds of the character referred to, such as "old papers" or similar papers, "broke" or the like.

When I use the word "paper" herein, I use it in the broad sense to include products of manufacture of all types and of all weights and thicknesses, which contain as an essential constituent a considerable amount of prepared fibre and which are capable of being produced on a Fourdrinier, cylinder, or other forming, felting, shaping or molding machine.

Cross reference is hereby made to my copending application Serial No. 640,330, filed October 29, 1932, which discloses substantially unsized paper, and all subject matter relating to substantially unsized paper therein is hereby made a part of the disclosure hereof.

By the term "wet end of the paper machine" I intend to include those instrumentalities employed in paper manufacture by which and/or in which a relatively concentrated paper mix is diluted, and treated, conveyed or fed up to the point of web-formation such as the mixing box, regulating and proportioning devices, rifflers, troughs, screens, head boxes, inlets, and the like, including also instrumentalities used in the white water cycle.

The term "fibrous mix" or "paper mix" as used herein is intended to mean a mix of various constituents including fibre from which paper may be made, either alone or after the addition of other ingredients.

By the expression "preponderating amount" I means an amount more than fifty-five per cent of the total.

As is well known, the term "casein" is commonly used to include casein of animal origin such as is found in or derived from the milk of mammals as well as plant or vegetable casein such as is found in or derived from certain legumes, leguminous plants, leguminous seeds (pulses) and the like, such as peas, beans, lentils, soy or soya beans, or the like (see e. g. "Casein" by E. L. Tague, Van Nostrand Co. N. Y. 1926, top of page 3). The chemical composition of the caseins derived from the milk of various mammals is thought to differ somewhat, as do the compositions of the caseins prepared by different methods from the milk of the same mammal. Likewise the composition of plant or vegetable caseins differ among themselves as well as from animal casein. Thus it is to be understood that in employing the word "casein" in the claims I do not confine myself to any particular material of exact composition, but rather use it to designate the protein or proteins, whether it be the animal or plant or vegetable protein or proteins, included broadly under the generic term "casein" as indicated above, or material derived from said protein or proteins. Moreover, where in the claims I use the word "casein", I use it in the generic sense to include casein and/or any compound or derivative thereof such for example as those indicated below. Likewise where in the claims I use the words "saponifiable material' or "rosin", I use them in the generic sense. Thus, in the case where reference is made to the addition of size containing "casein", "saponifiable material" or "rosin", the size may comprise such material in the form of an alkaline compound or derivative or the like; and in the case of size after incorporation in the paper, the incorporated size may comprise such material in the form of an aluminum compound or derivative or the like, resulting from the action of a precipitant such as alum.

While I have described in detail the preferred embodiment of my invention, it is to be under-

stood that the details of procedure, the proportions of ingredients, and the arrangement of steps may be widely varied without departing from the spirit of my invention or the scope of the subjoined claims.

I claim:

1. In a process of manufacturing paper wherein a paper mix containing fibrous material and alkaline filler is prepared and then run off on a web-forming device and wherein there is added size, the improvement which comprises adding size comprising saponifiable material and casein.

2. In a method of manufacturing paper filled with alkaline filler, the step of adding to the paper mix from which said paper is to be made size comprising saponifiable material and casein.

3. In a method of manufacturing paper filled with alkaline filler, the steps of adding to the paper mix from which said paper is to be made size comprising saponifiable material and casein, and a precipitant for said size.

4. In a method of manufacturing paper filled with alkaline filler, the step of adding to the paper mix from which said paper is to be made a size the component ingredients of which include substantially water insoluble saponifiable material and casein.

5. In a method of manufacturing paper filled with alkaline filler, the step of adding to the paper mix from which said paper is to be made a size the component ingredients of which include rosin and casein.

6. In a method of manufacturing paper filled with alkaline filler, the step of adding to the paper mix from which said paper is to be made a rosin size containing casein.

7. In a method of manufacturing paper filled with alkaline filler, the steps of adding to the paper mix from which said paper is to be made a rosin size containing casein, and a precipitant for said size.

8. In a method of manufacturing filled paper wherein a fibrous mix is run off on a web-forming device to form a web and wherein alkaline filler is employed, the step which comprises applying to said web on the paper machine size comprising saponifiable material and casein.

9. In a method of manufacturing paper filled with alkaline filler wherein a fibrous mix containing alkaline filler is run off on a web-forming device, the step which comprises applying to the fibrous web containing alkaline filler size comprising substantially water insoluble saponifiable material and casein.

10. In a method of manufacturing paper filled with alkaline filler wherein a fibrous mix containing alkaline filler is run off on a web-forming device, the improvement which comprises applying to the fibrous web containing alkaline filler size comprising saponifiable material and casein, and a precipitant for said size.

11. In a method of manufacturing paper filled with alkaline filler wherein a fibrous mix containing alkaline filler is run off on a web-forming device, the step which comprises applying to the fibrous web containing alkaline filler a size whose component ingredients include rosin and casein.

12. In a method of manufacturing paper filled with alkaline filler wherein a fibrous mix containing alkaline filler is run off on a web-forming device, the steps comprising applying to a fibrous web containing alkaline filler a size whose component ingredients include rosin and casein, and a precipitant for said size.

13. A product of manufacture comprising a casein-containing filled paper produced from a furnish comprising fibrous material, alkaline filler, and size comprising saponifiable material and casein.

14. A product of manufacture comprising a casein-containing filled paper produced from a furnish comprising fibrous material, alkaline filler, size comprising saponifiable material and casein, and a precipitant for said size.

15. A product of manufacture comprising a casein-containing filled paper produced from a furnish comprising fibrous material, alkaline filler, and a rosin size containing casein.

16. A product of manufacture comprising a casein-containing filled paper produced from a furnish comprising fibrous material, alkaline filler, a rosin size containing casein, and a precipitant for said size.

17. Filled paper comprising fibrous material, alkaline filler, and sizing comprising saponifiable material and casein.

18. Filled paper comprising fibrous material, alkaline filler, and sizing comprising rosin and casein.

19. Filled paper comprising fibrous material, alkaline filler, and sizing on the surface comprising saponifiable material and casein.

20. Filled paper comprising fibrous material, alkaline filler, and sizing on the surface comprising rosin and casein.

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