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PAPER MANUFACTURE

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My invention relates to the manufacture of paper, and has for its general object improvement in the arrangement and uniformity of distribution of paper fibers in the formation of the paper web; specific objects are: To secure good formation in papers made of long fibered stocks, such as Manila fibers, and to produce long-fiber papers having a soft, cloth-like "feel"; to produce papers having low air-resistance from hydrated stocks, and to improve the formation of papers made from short-fibered stocks such as sulfite and soda pulp. The term "formation" as used herein connotes the fixed disposition of the fibers of a sheet of paper and includes all effects produced in the arrangement of the fibers before the sheet passes over the drying rolls, exclusive of marks produced by dandy rolls.

Whatever may be the character of paper making fibers, the material of which they are composed, their average length, individual peculiarities of structure, etc., etc., uniform distribution of fibers in the web made therefrom on a paper machine is a desideratum; departures from desired or necessary uniformity of distribution may be broadly designated as flocculation, and that term is used herein as signifying the reverse of uniformity of fiber distribution in the formation of a paper web. Sundry correctives of flocculation have been long employed in paper manufacture, as for instance hydration of cellulose fibers in varying degree, or the mixture with processed pulps of varying proportions of ground wood, or the reduction of the average fiber-length, as by a jordan, but all such measures, corrective of flocculation in paper formation, tend to produce in some measure undesirable qualities in the paper product, which would not characterize it, if a practically perfect uniformity of arrangement and distribution of the chief fiber constituent of the paper mix could be secured without resort to such correctives, all of which are compromise measures, introducing relative defects in some degree, which have to be balanced against the advantage of uniform fiber distribution.

Probably the most striking example of fiber flocculation in paper manufacture is furnished by paper made of fibers longer than the normal, which flocculate before and during web formation and do not respond to the corrective measures such as are above mentioned, as do paper fibers of much shorter average length. Another example is supplied by wool fibers, which have a serrated structure, and have practically defied all attempts to make paper thereof. Also, fibers

composed of material having specific gravity of pronounced difference from unity (water) so strongly tend toward flotation or sedimentation in mass as to flocculate excessively during any attempt at paper web formation, and are therefore practically unavailable unless mixed with fibers of other material which when incorporated in the paper measurably degrade the qualities it would possess in full, were the paper to be constructed of unadulterated fiber. Asbestos paper, in which asbestos fiber is customarily adulterated with vegetable-derived pulp, is a well known example.

Paper fibers, of whatever nature, can be well dispersed and distributed in an abundant and well stirred body of water as the dilute mixture reaches the "wet end" of the paper making apparatus just prior to arrival at the web-forming part of the same, and by the employment of the invention herein to be described this uniform dispersion of fibers is conserved during web formation and flocculation greatly reduced, if not wholly prevented.

In an application for United States Letters Patent filed concurrently herewith and serially numbered 714,456, I have set forth and described a deflocculent gum-derivative and the method of making it. This gum-derivative is the deflocculant material employed by me in the practice of the invention herein described, which comprises the method of paper-making characterized by the use of the said gum-derivative as a fiber deflocculant, and includes also the stage product in paper making comprising a fiber mix containing the said deflocculent dispersed in the water, and the paper comprising fibers and the residue of said deflocculant left in the paper after it has become a finished product.

The deflocculent material which figures as a factor in the improvement in paper manufacture herein described, is a derivative from a poly-acetylated gum, specifically the commercial gum karaya which, as set forth in the Journal of the Chemical Society; Transactions, Vol. 89, pt. 2, pp. 1495 to 1505,—1906, is a tetra-acetyl derivative of cochlosperminic acid. Gum karaya is a natural product obtained from the plant *Cochlospermum gossypium* and allied botanical species, and of itself when dispersed in water manifests so little deflocculating or dispersive potency as to be practically a negligible factor for such purposes.

Gum karaya gives physical evidence that its molecular weight is very high, and its molecule very large. Though insoluble in water, it imbibes

water and forms a jelly therewith. Two per cent. of the gum in water forms a quite solid jelly, this jelly, however, manifests little coherence; it breaks "short", and dispersions of low concentration show no, or feeble dispersing potency in relation to particles suspended in water.

On treating a gum karaya dispersion in water with a mild alkali (preferably ammonia) the gum is hydrolyzed, but only to the extent of replacing all or part of the acetyl radicals constituent in it. Deacetylation of gum karaya produces a derivative thereof which is a water-dispersible gum (not water-soluble, as evidenced by its resistance to filtration, which is practically the same as that of karaya jelly) having the property of coherence in high degree and having marked deflocculating potency.

If a dry deacetylated gum karaya is desired, it may be obtained by mixing granulated karaya with ethyl alcohol (in which the gum is insoluble, and which causes little if any swelling of the gum) and then treating the mixture with alcoholic ammonia, which deacetylates the gum, filtering, washing the gum with alcohol to remove ammonium acetate, and drying. This deacetylated karaya, when dispersed in water, yields dispersions or jellies having the same properties as the karaya derivative produced as above described by deacetylation in water with dilute ammonia. Deacetylation can also be effected by treating granulated karaya with ammonia vapor.

Since commercial gum karaya is a mixture of gums collected not only from the plant *Cochlospermum gossypium* but from several other specifically different though allied species, all of which gums respond qualitatively alike to the action of mild alkali, and definitely undergo deacetylation in such treatment, I use the commercial term "gum karaya" herein as designating any poly-acetyl derivative of a gum acid or acids allied with cochlospermic acid, having regard to the observable physical characteristics of the deacetylated product rather than to a precise, (and as yet unascertained so far as I know) chemical analysis and identification of what is probably a miscellany of gums which are evidently closely related to each other in molecular structure and composition.

As set forth in the said copending patent application, I have discovered that by treatment of gum karaya with a mild alkali, preferably dilute ammonia, the gum karaya is wholly or partly deacetylated, remaining otherwise unaltered in the essentials of its nuclear molecular structure, and that the said partly or wholly deacetylated gum karaya is a hydrophile gum derivative possessing marked coherence and identifiable by its ability to form a coherent, stringy, tacky precipitate with ethyl alcohol from a water dispersion.

To make the deacetylated derivative of karaya gum, form a jelly with two parts by weight of the dry gum and 98 parts water. Excessive grinding of the gum is to be avoided, because mechanical attrition tends to degenerate it and prevent the formation of the characteristic stiff jelly. Excessive mechanical agitation or stirring of the jelly itself has the same tendency. The two per cent. dispersion of karaya in water is a quite stiff jelly, which, however, breaks "short", and manifests no stringiness or tackiness. To each 100 parts of this karaya jelly add 0.6 part of 26° Bé. aqueous ammonia, or add ammonia in the same ratio to the water in which the karaya is dispersed. The ammonia, being well mixed with the water and dispersed gum, in from two to three hours at room

temperature converts the gum jelly into a deacetylated derivative thereof which possesses pronounced cohesion, and is stringy, fibrous, or ropy in structure. The chemical change produced by the above indicated treatment of karaya is deacetylation. Titration shows that the amount of ammonia consumed in the process is equivalent to the amount of ammonium acetate formed, and that the change is not due to formation of an ammonium salt of the gum acid, or to amination of the gum, but to deacetylation of the karaya; this selective hydrolysis of the karaya is accompanied by no evidence of alteration of the complex molecular nucleus of the gum.

The physical characteristics of the deacetylated karaya derivative and the contrast between it and karaya may be demonstrated by a precipitation test with ethyl alcohol. If to a 2% dispersion of karaya in water there be mixed an equal volume of ethyl alcohol, the gum comes down as a fine flocculent precipitate, whereas similar alcohol treatment of the deacetylated karaya produces a tough, fibrous, stringy precipitate.

There is good evidence that the physical characteristics of the deacetylated but otherwise unaltered karaya are due mainly, if not wholly, to an emphatic polarity of the molecule of the gum-derivative, which the molecule of the original karaya does not possess. In other colloidal substances there may be observed the capacity to form strings or fibers, e. g., glue and other proteins, the molecules of which have acidic groups and basic groups in the molecule-chains. In karaya there is a potentially active carboxyl group, and hydroxyl groups which have been rendered inactive by association with acetyl groups, so that the molecules are only feebly polar, if at all, and incapable of orienting themselves. After deacetylation of karaya, free and active hydroxyl groups are present, and each molecule becomes emphatically polar, having positive hydroxyls and negative carboxyls, and orient themselves accordingly. This increase in molecular polarity is shown by the electro-conductivity of a dispersion of deacetylated karaya (washed to remove electrolytes), which is higher than that of a karaya dispersion, and is manifested by the stringy structure of the alcohol precipitates, in which the oriented arrangement of strongly polar molecules in the water-dispersion persists. This behavior also indicates a strongly probable reason why a karaya derivative produced by hydrolyzation to the extent of 25% of the total of acetyl groups (assuming that karaya is wholly a tetra-acetyl gum-acid compound) is, as has been observed and determined, as effective a deflocculant of water-suspended paper fibers as a more completely deacetylated derivative.

This deacetylated gum karaya manifests strong potency as a deflocculant or a dispersing agent of bodies such as fibers which are suspended in water wherein also the said deflocculant gum derivative is colloiddally dispersed. Relatively long fibers suspended in the water of a paper mix, which by reason of their length and tendency to entangle with each other and form flocks will, if the said deflocculant gum derivative be added to the mix, be thereby maintained in dispersion and will, upon formation of the paper web as upon a Fourdrinier wire or other web-forming instrument, be distributed thereon uniformly and without the deposition of flocks; and paper so made will be free from the mottled appearance and irregular formation which otherwise would characterize it. Thin papers of the tissue class

formed by the deposition in the web of the long fibers distributed and prevented from flocculating by the aid of the said deflocculant gum derivative, possess, by reason of the length of the fibers, unusual strength.

The deflocculating efficacy of the said deflocculant gum karaya derivative may easily be demonstrated in the following manner: A suspension of relatively long fibers (e. g., Manila fibers) in water is easily picked up by means of a stirring rod because of the flocculent entanglement of the fibers with each other; but if a small quantity of deacetylated gum karaya be introduced into the water wherein the fibers are suspended, it will be found difficult to pick up any substantial amount of the fiber by means of the stirring rod. In the case of Manila paper fibers, a dispersion of 10% or less of the said gum (dry weight) on the weight of the fiber in the paper mix, will be found sufficient to effect a satisfactory deflocculation and conserved dispersion of the fibers and to render the formation of the web practically perfect.

In making paper from relatively short fibers, the contrast between formation with and without the above-described deflocculant gum derivative is not so striking as in the case of long-fibered paper, but the employment of the said deflocculant enables the paper manufacturer to dispense with the correctives of poor web-formation heretofore used, and to avoid the defects in his paper product which have heretofore been tolerated for the sake of good formation.

An example of preparation of paper-fiber deflocculant and its employment in paper making, is as follows:

Disperse 100 pounds of dry karaya gum in about 5,000 pounds of water to which 30 pounds of 26° Bé. ammonia has been added. Mix (avoiding violent agitation) until the dispersion is free from lumps. This dispersion, containing about 2% of gum solids, is then allowed to age for about three hours, when optimum deacetylation should be complete, and is then further diluted with about 35,000 pounds of water, and allowed to stand at least half an hour. This dilute dispersion of karaya derivative is then metered into the paper stock stream, preferably as near the head box as possible. The amount is variable, according to the requirements of different paper stocks. In general, two per cent. of the gum-derivative solid on the weight of the fiber represents a maximum requirement for any of the usual paper-making fibers. It is believed to be preferable not to introduce this deflocculant at any point in the progress of the stock where it would be subjected to violent agitation or mechanical attrition.

I claim:

1. Method of making paper, characterized by adding to a fiber-mix before the formation of a paper web therefrom, of a water-dispersible water-imbibing polar-molecule derivative of a water-imbibing non-polar-molecule gum.

2. Method of making paper, characterized by adding to the fibrous mix before formation of a paper web therefrom, as a fiber deflocculant, deacetylated, water-imbibing, gum karaya.

3. Method of making paper, characterized by adding to the fibrous mix before formation of a paper web therefrom, as a fiber deflocculant, partly deacetylated, water-imbibing, gum karaya.

4. Method of making paper, characterized by adding to a mix of fibers of such character as normally tend to flocculate in paper formation,

before the formation of a paper web therefrom, a water dispersible water-imbibing polar-molecule derivative of a water-imbibing non-polar-molecule gum.

5. Method of making paper, characterized by adding to a mix comprising fibers of such character as will normally flocculate in paper formation, prior to the formation of a paper web therefrom, as a fiber-deflocculant, water-imbibing, deacetylated, gum karaya.

6. A product, more especially for use in the manufacture of paper, comprising fibers suspended in water; and a fiber deflocculant consisting of a water-dispersible water-imbibing polar-molecule derivative of a water-imbibing non-polar-molecule gum.

7. A product, more especially for use in the manufacture of paper, comprising fibers suspended in water, and a fiber deflocculant consisting of water-imbibing partly deacetylated, gum karaya.

8. Paper comprising fibers deflocculated and distributed, and characterized by containing a deflocculant consisting substantially of a water-dispersible water-imbibing polar-molecule derivative of a water-imbibing non-polar-molecule gum, and the residue of said deflocculant.

9. Paper, comprising fibers deflocculated and distributed, and characterized by containing a deflocculant consisting substantially of water-imbibing deacetylated gum karaya, and the residue of said deflocculant.

10. Paper, comprising fibers deflocculated and distributed, and characterized by containing a deflocculant consisting substantially of water-imbibing partly deacetylated gum karaya, and the residue of said deflocculant.

11. A stage product in the manufacture of paper, comprising fibers suspended in water, said fibers being of such length as will normally flocculate in paper formation, and a fiber deflocculant consisting of a water-imbibing deacetylated, gum karaya.

12. A stage product in the manufacture of paper, comprising fibers suspended in water, said fibers being of such length as will normally flocculate in paper formation, and a fiber deflocculant consisting of water-imbibing, partly deacetylated, gum karaya.

13. Paper, comprising fibers of such length as will normally flocculate in paper formation, deflocculated and distributed by means of a deflocculant consisting of water-imbibing deacetylated gum karaya, and the residue of said deflocculant.

14. Paper, comprising fibers of such length as will normally flocculate in paper formation, deflocculated and distributed by means of a deflocculant consisting of water-imbibing, partly deacetylated gum karaya, and the residue of said deflocculant.

15. A product more especially for use in the manufacture of paper, comprising fibers suspended in water, and a fiber deflocculant of water-imbibing, deacetylated gum karaya.

16. A product more especially for use in the manufacture of paper, comprising fibers suspended in water, and a fiber deflocculant of water-imbibing, partly deacetylated gum karaya.

17. Method of making a felted fibrous structure, from an aqueous suspension of fibers, which comprises adding to the fibrous suspension, before formation of the felted structure therefrom, water-imbibing, partially deacetylated gum karaya.

18. Method of making a felted fibrous structure, from an aqueous suspension of fibers, which comprises adding to the fibrous suspension, before formation of the felted structure therefrom, water-imbibing deacetylated gum karaya.
19. A stage product in the manufacture of a

felted fibrous structure, comprising a water suspension of fibers, said fibers being of such length as would normally flocculate, and a fiber deflocculant consisting substantially of water-imbibing deacetylated gum karaya.

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