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PAPER MANUFACTURE

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

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

An important object is the use of rubber as the sizing agent.

A further object is the employment of rubber in conjunction with rosin size as the sizing agent.

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 with rubber of paper filled with alkaline filler.

A further object is the employment of heat in the development of the sizing in paper sized with rubber and filled with alkaline filler.

A further object is the use of rubber or rubber-like materials containing softeners or materials which lower their melting and/or softening point.

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

It is well known that paper sized with rosin size in the ordinary manner will not serve to produce satisfactorily sized paper filled with alkaline filler. Special methods, however have been developed for this purpose which are disclosed in numerous copending applications of Rafton. A number of these methods are practical embodiments of the principle of minimizing the time and/or intimacy of contact of the constituents of an alkaline filler paper mix. Other methods involve the use of a hydrocarbon substantially inert to acidic and alkaline materials such as paraffine or the like, employed jointly if desired with one or more embodiments of the minimizing principle mentioned above.

It has hitherto been proposed to use rubber in paper mixes particularly in the form of dispersions such as natural latexes or artificial aqueous dispersions, but it has never been previously disclosed that such dispersions of rubber are suitable for sizing paper filled with alkaline filler. However we have now found that under certain conditions they will so serve.

The prior disclosed uses of rubber dispersions have been alleged to impart certain rubber-like qualities to the paper made therefrom, but the sizing effect obtained when rubber dispersions have been used in amounts which customarily are employed when rosin sizing is used for sizing paper, e. g. in the neighborhood of a few percent, has been rather poor. We have found, however, that even the relatively poor sizing which is obtained from the use of rubber in paper mixes is substantially deteriorated by alkaline filler, resulting in substantially unsized paper being produced therefrom. Practically the same result is obtained with rubber and alkaline filler as when rosin size is used therewith in the ordinary manner as referred to above.

We have found, however, that if rubber be incorporated into a fibrous mix with alkaline filler, applying the embodiments of the minimizing principle as set forth in the various Rafton applications, that sized paper filled with alkaline filler and with rubber as a sizing agent can be produced.

We have further found that papers filled with alkaline filler and containing rubber, and which are substantially unsized, because the embodiments of the minimizing principle were not employed in the manufacture thereof, may be converted in some degree into sized papers by aging. We have also found that this process may be accelerated and improved by the application of moderate heat, and greatly accelerated and improved by the application of still higher temperatures. Thus papers containing alkaline filler and rubber which are substantially unsized can be subjected to a temperature of, for example, from 140–150° C., and converted into sized paper. While this may be conducted as an operation independent of the paper-making operation, it is not necessary so to do, as this heating can be applied during the course of manufacture of the paper on the paper machine by suitable means.

As will be apparent, heating to such a temperature usually requires special apparatus and may in certain cases injure the fibrous material. We have found, however, that if modifying or softening agents be added to the rubber, such as those which cause it to melt, soften or spread at a lower temperature, that sizing in paper filled with alkaline filler may be obtained at a temperature such as will not substantially injure the fibre. Likewise by using other rubber-like materials which melt, soften or spread at a lower temperature than rubber, such as balata, gutta-percha, chicle or the like, satisfactory sizing may be obtained at substantially non-injurious temperatures. It will be understood that modifying or softening agents may likewise be applied to these last mentioned rubber-like materials with beneficial results. By these methods greatly improved sizing results may be obtained in papers filled with alkaline fillers.

In Rafton's various copending applications he has discussed in full the basis of the "minimizing principle", which phrase merely serves as an abbreviation of the longer expression "minimizing the time and/or intimacy of contact of the constituents of the mix". Briefly it 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 may be one which is actually acid, and/or one which, such as a size precipitate, 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 this principle a practical application has been developed whereby by minimizing the time and/or intimacy of contact of the acidic and alkaline constituents, the acidic constituent and/or effect produced thereby is substantially preserved in an alkaline filler mix.

With the present types of paper machines and the present arrangement of apparatus usually employed in paper machine operation, the contact of the acidic material and the alkaine 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 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, that is, at the wet end of the paper machine, serves to substantially conserve the acidic material and or effect thereof in the fibrous mix.

We have found that the precipitated rubber in an alkaline filler mix or the precipitated rubber in combination or association with the precipitant, although it may not actually be acid, acts very similarly to the acidic material and ordinary size precipitates referred to above as its sizing effect is similarly deteriorated. However by utilizing the various procedures based on the minimizing principle as set forth in the above referred to Rafton copending applications, suitable sizing effect can be obtained. Enumerating these various procedures, there are involved among others the following illustrative combinations:

Illustrative combination	Materials added in beater	Materials added at dilute stage
#1	Fibrous material Size Size precipitant Alkaline filler	Restoring agent
#2	Fibrous material Size Alkaline filler	Size precipitant
#3	Fibrous material Alkaline filler	Size Size precipitant
#4	Fibrous material Alkaline filler	Size precipitated by size precipitant
#5	Fibrous material Size Size precipitant	Alkaline filler
#6	Fibrous material Size precipitant	Size
#7	Fibrous material Size	Alkaline filler Size precipitant
#8	Fibrous material	Alkaline filler Size Size precipitant
#9	Fibrous material	Alkaline filler Size precipitated by size precipitant Alkaline filler

In addition there are various other procedures also disclosed in Rafton's copending applications involving the general minimizing principle such as protecting alkaline filler by precipitating thereupon a temporarily protecting precipitate such as size precipitated by alum; temporarily reducing the pH of an alkaline filler by the addition of alum thereto; the incorporation of sizing in the paper web; the incorporation of filler in the paper web; and the like. All these procedures are applicable to the use of rubber in paper filled with alkaline filler. Thus in the present invention, where we refer to "size" in the illustrative combinations and in this paragraph, such size comprises rubber as defined herein, or rubber in combination with other sizes as set forth later herein.

Where we speak of the use of rubber in paper manufacture what we mean is the use of rubber dispersions preferably aqueous, which are capable of being mixed with a paper mix and/or applied to a web while the latter are in aqueous or wet condition. Such dispersions may be natural latexes or mixtures thereof, or artificially compounded natural latexes, or artificially prepared rubber dispersions, suitably preserved if desired, a number of which are known. When we use the word "rubber" we mean to include any rubber-like material such as substantially water insoluble gums such as chicle, balata, gutta-percha, or rubber, or substances containing or comprising rubber or rubber-like material, either natural or synthetic. We mean also to include compounds of rubber or rubber-like material, and materials which produce rubber or rubber-like material when suitably treated, such as in the paper mix or in the drying and/or heating of the paper. It should be understood, however, that the word "compounds" as used in the previous sentence as referring to rubber or rubber-like material does not have the same meaning as it has in certain other places in this specification where it, (or the associated adjectival form "compounding"), is used to refer to what is known colloquially in the rubber art as "a compound", i. e. a mix of rubber, fillers, softeners, vulcanizing agents and the like which is blended as in a rubber compounding mill and then undergoes final treatment to convert it into a final rubber or rubber-like article; on the contrary, the word is used in the previous sentence in its scientific meaning which includes any chemical or physico-chemical combination or association of rubber or rubber-like material with any element or chemical group or grouping, as well as any derivative thereof or of the original rubber or rubber-like material, and any associated molecular species such as polymer, isomer, tautomer, or the like.

In the preferred practice of our invention we start with fibrous material. To this a rubber dispersion may be added in the beater, or, in accordance with the various combinations and procedures referred to above, the rubber dispersion may be added at the dilute stage, or applied in the web. There may also be added a precipitant for the rubber dispersion or one need not be added. The absence of such precipitant will not result in the rubber dispersion being lost from the paper mix in the white water owing to it not being coagulated in the paper mix, because we have found that in general alkaline filler itself coagulates rubber dispersions. However a precipitant may be added with advantage in certain cases, and this may be added as noted in the several combinations and procedures outlined above either in the concentrated and/or in the dilute stage or in the web. Likewise fractional or step precipitation may be employed.

Likewise the alkaline filler may be added when the mix is either in the concentrated condition, or in the dilute stage, or in the web. In the cases where no size precipitant is desired to be used, the various combinations and procedures referred to above may still be employed, the only difference being that the size precipitant is omitted in such cases.

To illustrate concretely one specific example, fibrous material, alkaline filler and a rubber dispersion may be mixed in the beater and alum added thereto. The mix may pass through the various preparing machinery until it reaches the mixing box preparatory to passage on to the web-forming device. Preferably at this point or subsequent thereto is added a further quantity of alum which restores the sizing imparted by the rubber. The amount of alkaline filler used may vary as desired, for example, it may be approximately 15–20% of the furnish, the rubber may be about 2–4% on the dry basis, the original alum added may be about 3%, and the restoring alum added may be about 3%. These figures as well as others given herein are understood to be illustrative only and not limiting, as we have found various other proportions to be suitable for our purpose. It will be apparent, however, that where we use the expression "paper filled with alkaline filler" we mean filled paper which contains as an ingredient alkaline filler in appreciable amount, i. e. in an amount not less than that of the rubber present.

It will be understood that size or sizings other than rubber may be employed in combination with the rubber in practicing the various combinations and procedures outlined herein. Rosin size may with particular advantage be so employed. Wax emulsions, particularly paraffin wax emulsions, especially rosin size-paraffin emulsions, may also be employed with advantage.

One of the modifications wherein rosin size may be particularly advantageously employed is: an alkaline filler may be temporarily protected by precipitating thereon in a continuous manner approximately 5% of rubber from a dispersion with about 7½% alum, and the same added promptly at the wet end of the paper machine to a fibrous mix comprising fibre sized with rosin size and alum in the beater.

We have disclosed above that rubber-containing substantially unsized paper filled with alkaline filler, made without the employment of the minimizing principle, may be converted to sized paper by aging or preferably by heat. These procedures have also been found to improve the sizing of rubber-containing sized paper filled with alkaline filler, which have been made in accordance

with the minimizing principle. It is to be noted that the heating action may in some cases require an interval of time to develop, and hence several heating rolls are preferably used, or the paper may pass through a heated chamber. Of course the same result may be obtained after the manufacture of the paper by putting the paper through a special heating process.

As stated above when employing rubber with softening agents the temperature necessary to be obtained is reduced, and may be in many cases obtained directly on the paper machine without additional apparatus.

At times, especially when the temperature desired to be used is such as to tend to injure the fibrous material, such injury may be substantially lessened or even eliminated by conducting the heating in the presence of a substantially inert gas or even in a vacuum; or steam or other heating or curing means or procedures, including the application of pressure, may be employed which in some instances serve to reduce the temperature required.

Our invention may be used with or without vulcanizing agents. The vulcanizing agents may be separately incorporated in the paper mix or may be originally incorporated in the rubber dispersion, either with the already dispersed rubber, or directly with the rubber before the dispersion thereof if an artificial dispersion be employed. Softening agents may be added either in the paper mix, or blended directly with the rubber dispersion. Better results at times, however, seem to be obtained when the softening agent is added to the rubber prior to its dispersion, especially when artificial dispersions are employed. We may also if desired use accelerators or super-accelerators, a variety of which are well known, and these may be incorporated in various manners as indicated above. As will be understood the rubber may if desired be modified with other modifying or compounding agents ordinarily employed in compounding rubber.

As stated above in addition to rubber any other sizes suitable for use in paper may be employed, the most common of which is rosin size. Any proportions desired may be employed. Such sizes may be added to the paper mix with the rubber dispersion or independently as desired. Such sizes usually require precipitation such as with alum, in order to be rendered effective in the paper. One method which may be employed is to melt rubber and rosin together in the desired proportions, or to dissolve them in a common solvent, and preferably evaporate the solvent, and then emulsify in alkali. This gives a rubber-rosin size dispersion. In making up such a dispersion the modifying, softening, vulcanizing or other agents may be blended with the original rubber or rubber-rosin mix. In some cases it has been found that the presence of sizes other than rubber materially assisted in attaching the rubber to the fibres.

The preferred precipitant for the rubber and/or other size is alum, but a number of others may be employed, which need not be acidic for instance soluble salts of the alkaline earth metals, or of other metals, or acidic materials such as acetic acid or other organic or mineral acids, or acid or acid reacting salts. Any precipitant for rubber dispersions may serve. We employ the word "precipitant" as synonymous with "coagulant" and as embracing "agglomerant"

As examples of softening agents suitably employed may be mentioned petrolatum, stearic acid, cumarone resin, cottonseed oil, linseed oil, and the like, a variety of which are well known.

The term "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 term "alkaline filler" we 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 Rafton's U. S. Patent No. 1,595,416 of August 10, 1926; calcium carbonate magnesium hydroxide disclosed in Rafton's U. S. Patent No. 1,415,391 of 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.

When we use the word "paper" herein, we 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.

By the term "wet end of the paper machine", we 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, in-

cluding those instrumentalities used in the white water cycle.

Where in the claims we use the word "web", we mean to include not only the already formed web, after it has left the web-forming device, but also the forming web as it exists at any point on the web-forming device.

It is to be understood that our invention is not dependent upon or limited by any theory expressed herein.

We are aware that rubber has previously been compounded with alkaline materials that such compounded rubber has been aqueously dispersed, that rubber has been dispersed with alkaline agents, and other like procedures have been described; but so far as we know it has never been proposed to use aqueous rubber dispersions added in the liquid pulp or to the web in relatively minor proportions to produce a sized (i. e. ink-resistant) paper containing as filler alkaline filler in an amount not less than, or in excess, and normally in considerable excess, of the rubber present.

We have referred to various copending applications of Rafton above. Cross reference is hereby made particularly to the following: application Serial No. 262,030, filed March 15, 1928, now matured into Patent No. 1,819,441, issued August 18, 1931; application Serial No. 304,167, filed September 5, 1928; application Serial No. 304,168, filed September 5, 1928; application Serial No. 304,170, filed September 5, 1928; application Serial No. 304,172, filed September 5, 1928; application Serial No. 304,173, filed September 5, 1928; application Serial No. 304,175, filed September 5, 1928; application Serial No. 304,176, filed September 5, 1928; application Serial No. 304,177, filed September 5, 1928, now matured into Patents Nos. 1,803,642; 1,803,643; 1,803,645; 1,803,647; 1,803,648; 1,803,650; 1,803,651 and 1,803,652, respectively, all issued May 5, 1931; application Serial No. 319,719, filed November 15, 1928; application Serial No. 319,720, filed November 15, 1928; application Serial No. 319,721, filed November 15, 1928; application Serial No. 321,753, filed November 24, 1928; application Serial No. 321,754, filed November 24, 1928, now matured into Patents Nos. 1,808,067-71, respectively, all issued June 2, 1931; application Serial No. 353,668, filed April 8, 1929, now matured into Patent No. 1,848,659, issued March 8, 1932; application Serial No. 428,231, filed February 13, 1930; application Serial No. 440,645, filed March 31, 1930; application Serial No. 501,674, filed December 11, 1930; application Serial No. 533,571, filed April 28, 1931; application Serial No. 533,872, filed April 29, 1931; application Serial No. 534,461, filed May 1, 1931; application Serial No. 534,462, filed May 1, 1931.

Whereas we have described in detail the preferred embodiments of our invention, it is to be understood that the details of procedure, the proportions of ingredients, and the arrangement of steps may be widely varied without departing from the spirit of our invention or the scope of the subjoined claims.

We claim:

1. Paper filled with alkaline filler comprising fibrous material, rubber, and alkaline filler.

2. Sized paper filled with alkaline filler comprising fibrous material, rubber, and alkaline filler.

3. Paper filled with alkaline filler comprising fibrous material, precipitated rubber, and alkaline filler.

4. Paper filled with alkaline filler comprising fibrous material, rubber, and a modifying agent therefor, and alkaline filler.

5. Paper filled with alkaline filler comprising fibrous material, rubber, and alkaline filler, said rubber comprising balata.

6. Paper filled with alkaline filler comprising fibrous material, rubber, and alkaline filler, said rubber comprising gutta percha.

7. Paper filled with alkaline filler comprising fibrous material, rubber, and alkaline filler, said rubber comprising chicle.

8. Paper filled with alkaline filler comprising fibrous material, rubber, vulcanizing material, and alkaline filler.

9. Paper filled with alkaline filler comprising fibrous material, rubber, and a softening agent therefor, and alkaline filler.

10. Paper filled with alkaline filler comprising fibrous material, rubber, and alkaline filler, said alkaline filler comprising calcium carbonate.

11. Paper filled with alkaline filler comprising fibrous material, rubber, and alkaline filler, said alkaline filler comprising calcium carbonate and magnesium compound.

12. Paper filled with alkaline filler comprising fibrous material, rubber, and alkaline filler, said akaline filler comprising calcium carbonate magnesium hydroxide.

13. Sized paper filled with alkaline filler comprising fibrous material, rubber, and alkaline filler, said alkaline filler being present in excess of said rubber.

14. Sized paper filled with alkaline filler comprising fibrous material, rubber, size, and alkaline filler.

15. Sized paper filled with alkaline filler comprising fibrous material, rubber, precipitated size, and alkaline filler.

16. Sized paper filled with alkaline filler comprising fibrous material, rubber, precipitated rosin size, and alkaline filler.

17. Sized paper filled with alkaline filler comprising fibrous material, rubber, rosin size precipitated by alum, and alkaline filler.

18. Sized paper filled with alkaline filler comprising fibrous material, rubber, precip-

itated rosin size, and alkaline filler, said alkaline filler being present in excess of said rubber.

19. A method of manufacturing sized paper filled with alkaline filler characterized by the inclusion in a paper furnish of alkaline filler and rubber.

20. A method of manufacturing sized paper filled with alkaline filler characterized by the inclusion in a paper furnish of alkaline filler, rubber, and a precipitant.

21. A method of manufacturing sized paper filled with alkaline filler characterized by the inclusion in a paper furnish of alkaline filler, rubber, and size.

22. A method of manufacturing sized paper filled with alkaline filler characterized by the inclusion in a paper furnish of alkaline filler, rubber, size, and a precipitant.

23. A method of manufacturing sized paper filled with alkaline filler characterized by the inclusion in a paper furnish of alkaline filler, rubber, and rosin size.

24. A method of manufacturing sized paper filled with alkaline filler characterized by the inclusion in a paper furnish of alkaline filler and rubber, and the applying of heat sufficient to develop sizing in said paper.

25. In a method of manufacturing sized paper filled with alkaline filler in which material is added under conditions favoring the minimizing of the time and/or intimacy of contact of the constituents of the mix, that step comprising the inclusion of rubber in the paper mix.

26. In the method of manufacturing sized paper filled with alkaline filler in which material is added under conditions favoring the minimizing of the time and/or intimacy of contact of the constituents of the mix, those steps comprising the inclusion of rubber and a precipitant in the paper mix.

27. In a method of manufacturing sized paper filled with alkaline filler in which material is added under conditions favoring the minimizing of the time and/or intimacy of contact of the constituents of the mix, those steps comprising the inclusion of rubber and size in the paper mix.

28. In the method of manufacturing sized paper filled with alkaline filler in which material is added under conditions favoring the minimizing of the time and/or intimacy of contact of the constituents of the mix, those steps comprising the inclusion of rubber, size, and precipitant in the paper mix.

29. In a method of manufacturing sized paper filled with alkaline filler in which material is added under conditions favoring the minimizing of the time and/or intimacy of contact of the constituents of the mix, those steps comprising the inclusion of rubber and rosin size in the paper mix.

30. In a method of manufacturing sized paper filled with alkaline filler in which material is added under conditions favoring the minimizing of the time and/or intimacy of contact of the constituents of the mix, those steps comprising the inclusion of rubber and rosin size and a precipitant therefor in the paper mix.

31. In a method of manufacturing sized paper filled with alkaline filler in which material is added under conditions favoring the minimizing of the time and/or intimacy of contact of the constituents of the mix, those steps comprising the inclusion of rubber in the paper mix and the application of heat sufficient to improve the sizing in said paper.

In testimony whereof we affix our signatures.

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