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PAPER MANUFACTURE

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My invention concerns the manufacture of paper.

The principal object of my invention is to provide a process of manufacturing paper filled with alkaline filler, and to obtain the paper made by said process.

An important object is to provide a process for the manufacture of paper filled with alkaline filler, said paper being sized to any desired degree, and to obtain the paper made by said process.

A further object is to provide a process for the manufacture of paper filled with alkaline filler, said paper being sized to any desired degree, wherein the sizing effect is obtained by the joint use of materials comprising a sizing material and a copper compound, and to obtain the paper made by said process.

A further object is to provide a process for the manufacture of paper filled with alkaline filler wherein there are employed materials comprising a sizing material and a copper compound, particularly a substantially water-soluble copper compound, and to obtain the paper made by said process.

A further object is to provide a process for the manufacture of paper filled with alkaline filler wherein there are employed materials comprising rosin size and a substantially water-soluble copper compound, for example copper sulphate, and to obtain the paper made by said process.

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

As is well known, certain precautions must be taken in the use of certain filler substances in papermaking, and particularly in sizing papers in an alkaline medium as in the case when alkaline filler is employed. In the past it has been considered impossible to size paper filled with alkaline filler. However comparatively recently the sizing of paper filled with alkaline filler has been accomplished by several newly introduced processes, e. g. by the use of wax emulsions, or by temporarily lowering the alkalinity by use of an acid salt and allowing the sizing agent to precipitate before the full chemical action between the acid salt and the alkaline filler might have taken place, and the like. Some sizing results have been effected by the above referred to processes, but I have devised a process which gives improved results and which is wholly different.

In the manufacture of paper filled with alkaline filler, I use in conjunction with a sizing material a substantially water-soluble copper compound. This copper compound either completely replaces the alum, which is universally used in paper-making with sizing material, or is used together with alum. However the use of such a copper compound gives results wholly different from those obtained by the use of alum. The copper compound in conjunction with the sizing material acts in a unique and wholly unexpected manner to impart sizing effect to paper filled with alkaline filler, e. g. under conditions where, with the same materials and in the absence of such a copper compound, the use of alum would not impart sizing effect.

My invention thus deals with an improved method of securing sizing effect in paper filled with alkaline filler. I have found that by employing various copper salts, particularly the sulphate, a superior sizing effect is obtained by the addition of amounts of copper sulphate up to 2% or 3% on the weight of the fibre and filler, and as low as $\frac{1}{10}$ of 1% on the weight of the fibre, varying the rosin size emulsion within about the same percentage range as the copper sulphate. Sizing results may be varied to any desired degree from complete waterproofing to only slightly sized effect by varying the amounts of sizing material and copper sulphate added to the papermaking materials. Thus it is apparent that 3% of substantially water-soluble copper compound, such as copper sulphate, and/or 3% of sizing material, such as rosin size, is not to be understood as an upper limit or limits, as naturally, if desired, any larger amount or amounts may be used in accordance, for example, with the results desired to be obtained.

In the application of size material in the presence of the alkaline filler, I have found that the sequence of adding the chemicals is of great importance. The preferred sequence, (P), and one by means of which excellent results are obtained is as follows, the material being added and mixed together in the order mentioned:

(P)

(1) Pulp
(2) Filler
(3) Size
(4) Copper sulphate
(5) Acidic material

An illustrative example of a formula embodying the above order of mixing is as follows:

30 parts by weight of pulp
10 parts by weight of alkaline filler suspended in 750 parts by weight of water
1 part by weight of size figured as dry rosin (but actually added as a water emulsion)
1 part by weight of copper sulphate
Acid to neutralize (phenolphthalein as indicator)

By employing the sequence (P) referred to above, I have found that a greater degree of sizing appears to be obtained than when for example the alkaline filler is first treated with acid, then the pulp added, then the size and finally the copper sulphate, which I may term sequence (Q). When the ink float test is applied to the paper

obtained from both sequences, the result of the test on the paper from the preferred sequence (P) is as high as 12 mins. 55 secs., whereas the result of the test from the paper obtained by employing the last mentioned sequence (Q) is 6 mins. 10 secs.

The following are the comparative results of ink tests when the ingredients are added in still other sequences, (A), (B) and (C), the sequence of addition being the order in which the materials are mentioned:

(A)

(1) Pulp
(2) Filler
(3) Copper sulphate
(4) Size
(5) Neutralizing agent (acidic material)

(B)

(1) Pulp
(2) Filler
(3) Copper sulphate
(4) Neutralizing agent (acidic material)
(5) Size

(C)

(1) Pulp
(2) Filler
(3) Size
(4) Neutralizing agent (acidic material)
(5) Copper sulphate

The comparative sizing tests of the papers made according to these three orders of addition were as follows:

(A) 25 secs.;
(B) 10 mins. 0 secs.;
(C) 5 mins. 0 secs.

Obviously, I do not limit my invention to any particular order of addition, as the above or any other order of addition of the ingredients may be used. For example, as is apparent, the pulp, size and copper sulphate, and if desired the acidic material also, may be first mixed together, or mixed together in any sequence, prior to the addition of the filler, and then the filler added. Also any two or more of the ingredients may be premixed, before admixture with one or more of the other ingredients. E. g. the substantially water-soluble copper compound and the size may be premixed prior to addition to the other ingredients, or copper resinate, previously made, may be added to the other ingredients, preferably in suitably dispersed form. Moreover the acidic material (neutralizing agent) may be entirely omitted, if desired. Also the entire quantity of any one ingredient need not be added all at once, but any ingredient may if desired be added in portions at more than one time, and if desired at more than one place in the papermaking process, and the addition of any ingredient may be made all at once, or in portions intermittently, or by continuous addition, as is well known in paper making.

Another example of a formula from which a paper may be made by my process is as follows:

	Per cent
Sulphite pulp	30
Alkaline filler (comprising calcium carbonate)	30
Soda pulp	30
Starch (plus coloring if desired)	5
Rosin size	2
Copper sulphate	3

The above materials constitute 5% of the total of which the other 95% is water, as is also the case in the preceding formulas, that is if the formula is prepared in the beater at the usual beater proportions of solids and water. However of course I do not limit myself to a mixture of the ingredients and water in such proportions, as I may use any proportions, e. g. such as may be customary in papermaking. The above illustrated example will give a well sized sheet of book paper. As shown previously, an acidic material may also be added if desired.

In practicing my invention, (e. g. as in the various sequences and formulas indicated above), the filler may be any alkaline filler, which may be untreated, or treated, e. g. as described later herein; and of course if desired other fillers may be used in addition to the alkaline filler, well known examples being clay, talc, calcium sulphate, barium sulphate and the like. Likewise the size may be any sizing material which is precipitable or affected by a substantially water-soluble copper compound; for example it may be in the form of a rosin soap containing about 70% saponified rosin and 30% free rosin.

The acidic material employed may be sulphurous acid. Calcium acid sulphite gives highly satisfactory results. Other acid materials may be employed, but it has been found that sulphurous acid and bisulphites produce a better sizing effect than sulphuric acid for instance. The acid material most commonly used in papermaking is alum, and in many instances I prefer to use it as my acidic material; or I may employ alum in combination with the various other acidic or other materials. Where I speak of "neutralizing" or "neutralizing agent," of course I do not ordinarily mean that any such large amount of acidic material is added as would be sufficient to react with all or with a large part or even with any substantial part of the alkaline filler, and thus destroy it or any large or substantial portion of it, as of course my invention concerns the manufacture of paper filled with alkaline filler. However if for some reason it be desired to employ an unusually large amount of acidic material, that still falls within the scope of my invention, provided that the paper made by the process still contains alkaline filler.

Where, as in the first illustrative formula given herein, I speak of "acid to neutralize (phenolphthalein as indicator)," I mean that the indicator is used to make the test as soon as the acidic material has been well incorporated in the mix. The pH of the mixture may be brought below 7, at least temporarily, if desired, but it does not necessarily have to be brought below 7; nor even down to or near 7. Moreover in respect to the acidic material, this may, as indicated in one of the illustrative formulas given herein, even be omitted in certain cases. I do not limit myself to any definite amount of acidic material as I may use an amount necessary to neutralize according to the test indicated above, or less than that amount, or more than that amount. Where I use acidic material, I usually find from about .5% to 5% (e. g. alum) calculated as dry weight on the dry weight of the ingredients of the mix to be a suitable amount to employ, but this range is to be understood to be illustrative only and not limiting as I may use more or less, as the occasion demands. Moreover, when used, the acidic material may be added in any order in respect to the other ingredients. It may also in certain cases, if desired, be mixed directly with the substantially water-soluble cop-

per compound prior to the addition of the copper compound to the papermaking mix.

Although I am not certain what the specific effect of the substantially water-soluble copper compound is, there are strong indications that this compound may prepare the fibre so that it receives the size more readily. It may be that cupric hydroxide is precipitated on the surface of the fibres as a protective gel which will absorb other colloidal materials from the same suspension. Another explanation may be that the precipitate of the rosin size (or other sizing material) with the substantially water-soluble copper compound, the composition of which rosin size precipitate depends among other things upon the composition of the rosin size used and the conditions under which the precipitate is formed—but which for the sake of convenience herein may be assumed to be copper resinate—is unaffected by alkaline filler or at least is far more resistant to the deteriorating or destructive effect of alkaline filler than is the precipitate produced by the action of alum on rosin size (i. e. an alum-rosin size precipitate), or other alum-size precipitate. Furthermore when the copper resinate or other substantially water-soluble copper compound-size precipitate or the like is co-precipitated or associated with an alum-rosin size precipitate, or other size precipitate, the copper resinate or the like may fortify or protect such size precipitate against the deteriorating or destructive action of alkaline filler. Or the substantially water-soluble copper compound may convert a forming or already formed alum-rosin size or other size precipitate into the more resistant copper resinate or other substantially water-soluble copper compound-size precipitate. However it is to be distinctly understood that these possible explanations of the reason why a substantially water-soluble copper compound appears to be effective in my process and the resulting compound or compounds in the paper made therein are only theory, and that regardless of the correctness or incorrectness of these or of any other theories purporting to explain its action, which have or may be advanced, my invention is entirely independent thereof, and is not to be limited or in any way restricted by these or any other theories, because the facts remain that the use of a substantially water-soluble copper compound in connection with a size in the manufacture of paper filled with alkaline filler does produce the distinctive and unique results herein described and not heretofore obtained.

The term "alkaline filler" has already acquired a definite meaning in the art, which may be briefly summarized as filler which is substantially water-insoluble, and which when agitated with freshly boiled distilled water imparts thereto a pH value greater than 7. (See for example Patent 1,808,067, June 2, 1931, page 3, lines 96 et seq.) Examples of fillers of this type are, as is well known, calcium carbonate, which may come from natural sources, from the lime sludge from the causticizing process, from precipitation of lime by carbon dioxide, or from other sources; magnesium carbonate; calcium carbonate magnesium hydroxide; calcium carbonate magnesium basic carbonate and the like; or mixtures or compounds of the above. Thus when I use the expression "alkaline earth metal," I mean to include magnesium within the scope of the expression. In any case, the alkaline filler may be used in the form as it occurs or is produced, or in a purified or specially prepared form, and it may have any desired particle size from relatively coarse, through the finer, and even down through the colloidal range, or a mixture of particle sizes, as desired.

In respect to the addition of materials in my process, I have given a preferred order (P). I have also stated, however, that any other order may be used. My invention, of course, may be practiced by addition of materials in the beater or other mixing machine, or if desired, may be practiced in connection with any of the now well known procedures for the manufacture of paper filled with alkaline filler, such for example as those mentioned in my discussion of prior processes given above, and specifically in accordance with the so-called "minimizing" procedures, which may be briefly described without going into details as addition of one or more materials late in the papermaking process. This addition may be made in one or more of the chests. Of the chests, it is preferable to make the addition in the machine chest (or what is substantially the equivalent, in the flow of the mixture of papermaking ingredients already added after it leaves the beater chest—if a beater chest be used—and before it is delivered into the machine chest). Or addition may be made, and this is preferable, in the dilute stage of the papermaking process such as at the mixing box, rifflers or headbox of the machine.

Thus, for example, the alkaline filler, the size, the substantially water-soluble copper compound, and the acidic material, if used, or any of them, or any part of any of them, (or fibrous material associated therewith, e. g. broke or old paper stock), may be added at any point in the papermaking process either in the beater or other mixing or treating device, or subsequent thereto up to the point of web formation. Moreover addition of such material may be made on the web itself, either while it is on the web-forming device, or subsequently. This, as well as the above procedures, are all now well known. If the addition is subsequent to the beater, such addition is preferably made continuously rather than intermittently. One illustrative example of practicing my invention in connection with a minimizing procedure is to add the pulp, size and substantially water-soluble copper compound in the beater, then add the alkaline filler in the beater, and then add alum later in the process, e. g. at the dilute stage. Another illustrative example is to add the pulp, size and substantially water soluble copper compound in the beater, and then add alkaline filler and alum later in the process, e. g. at the dilute stage.

Also, of course, any other procedures well known for use in the manufacture of paper filled with alkaline filler may be used in connection with the practice of my invention.

In respect to the cases where the substantially water-soluble copper compound is added prior to the addition of the sizing material and where the alkaline filler may also be present prior thereto, there will be more or less reaction between the copper compound and the alkaline filler, but because that is a reaction between a substantially water-soluble material (copper compound) and a substantially water-insoluble material (alkaline filler), it necessarily proceeds somewhat slowly. However, if there be present simultaneously with the alkaline filler, a sizing material such as rosin size, with which the substantially water-soluble copper compound reacts, the reaction of the substantially water-soluble

copper compound with the rosin size is rapid, if not in most cases practically instantaneous, because the rosin size is either in solution or in substantially colloidal solution. Therefore although there may be more or less reaction of the copper compound with the alkaline filler, depending on the time of contact of the two before the sizing material is present, nevertheless the preponderant part of the substantially water-soluble copper compound present if not substantially the entire amount, will react with the sizing material, especially if the sizing material in suitable amount be added with, or shortly after, the alkaline filler. However in all these cases the alkaline filler may have some joint or subsequent action on the substantially water-soluble copper compound-size precipitate. If the sizing material in suitable amount and the substantially water-soluble copper compound are present before the alkaline filler is added, of course the first two ingredients will react initially, and whatever action the alkaline filler may have will then take place subsequently. It may also be, as suggested above, that the substantially water-soluble copper compound may additionally act upon the fibrous material in a greater or less degree, or prepare the fibre in some way to receive the size. It should be understood, however, that these are merely theories, and that my invention is independent of their correctness or incorrectness.

It is well known to use all types of pulp with alkaline fillers, (for example, see Patent No. 1,595,416 of Aug. 10, 1926). For instance there may be used mechanical (i. e. groundwood pulp) or chemical wood pulp, rag pulp, straw pulp, esparto pulp, jute, hemp or asbestos or the like, or mixtures of one or more of these may be used. Of course my invention may be practiced with any of these or any other pulps used in the paper industry, all of which are well known. Of the well known chemical pulps there may be mentioned, as examples, soda pulp, sulphite pulp, sulphate or so-called kraft pulp, Keebra pulps, as well as semi-chemical pulps, and the like. These or any of them may be used as produced, or may be highly purified if desired such as in the case of "alpha" pulp, i. e., a pulp high in alpha cellulose content. Additionally of course reworked pulps such as old papers, either without deinking or after deinking may be used. Such old paper stock is commonly used. The waste paper of the papermaking process, the so-called "broke," may of course also be used as is customary in papermaking. Any of the pulps mentioned may be used either in unbleached, partly bleached or in bleached condition. The pulps may of course be used alone or admixed in any proportions as desired.

Likewise I may employ in my paper any desired proportion of alkaline filler to pulp, as is well known in the art, to obtain any percentage of filler in the resulting paper that I may desire. However in many cases I prefer to use the amount that will give me from 5-40% of alkaline filler in the resulting paper, generally 15-30% being a convenient amount.

As to sizing material, I prefer rosin size, and in the term rosin size I mean to include all the well known types of rosin size, whether made from rosin or synthetic rosin acid or acids, from the substantially wholly saponified sizes, such as the well known Delthirna size or the like, through the rosin sizes containing more or less free, i. e., unsaponified rosin, but which are predominantly saponified rosin, down to the sizes which may be preponderatingly or substantially completely in unsaponified condition, such as Bewoid size or the like. The rosin sizes used may be the ones made by treating rosin or the like with any suitable saponifying or emulsifying agent, such as an alkali, of which the alkaline sodium compounds are the commonest ones; or they may be made with alkaline potassium or ammonium compounds or ammonia or with an amine, all of which are well known for making rosin sizes. Or other well known emulsifying or treating agents such as casein, soluble oils, sulphonated higher fatty acids, or other sulphated or sulphonated products may be used with the rosin or the like, alone, or in conjunction with, or following, the agents previously mentioned. If desired the melting point of the rosin used may be lowered, as by fluxing with a material which will lower its melting point, such as an oil, e. g. mineral oil, or animal or vegetable oil, or by paraffin or the like. Where I use the word "resinate" herein, it refers to a derivative of rosin or synthetic rosin acid or acids.

In the place of rosin size, I may use any other suitable well known sizing materials which are used with alkaline filler, for example, the wax or paraffin emulsions mentioned previously herein, or oil emulsions, such as mineral oil emulsions, or petroleum jelly emulsions, all of which may if desired be conveniently made with rosin size as an emulsifying agent; or I may use organic material reactive with alkali such as a fatty acid, e. g. stearic, oleic, palmitic, linoleic, or the like, which may be hardened or hydrogenated if desired, in my size instead of rosin, which may be emulsified or treated if desired e. g. with any of the emulsifying or treating agents mentioned above in connection with rosin, and particularly if desired with an alkaline material such as an alkaline sodium, potassium, or ammonium compound, or ammonia, or an amine or the like.

Moreover certain pulps used in the papermaking process may contain more or less material as an integral part thereof which may impart a certain degree of sizing to ordinary paper made therewith (i. e., paper not containing alkaline filler), without the actual addition of sizing material itself in the papermaking process; or which may impart a degree of sizing to such paper which may be enhanced by the addition of other sizing material in the papermaking process. This may happen with certain groundwood pulps; and particularly with chemical or semi-chemical pulps made from resinous or similar woods, in which the resin or the like, which of course in part at least is of a nature somewhat akin to rosin, is not substantially, or not completely, removed by the chemical treatment the wood receives in the manufacture of the pulp or in the subsequent treatment of the pulp. An example of such an instance is in the case of certain pulps made particularly by the so-called sulphate or kraft process—particularly when the pulps are somewhat undercooked—where the kraft pulp may have a certain so-called self-sizing quality, that is to say, may impart a certain amount of sizing to the ordinary paper made therewith, without the addition of further sizing material. However in many such instances, further sizing material is used to enhance the sizing effect of the pulp itself. My invention may be used in connection with any such pulp containing sizing material as an integral part thereof, to obtain sizing effect or improve sizing effect when

alkaline filler is used therewith, the situation being the same in all respects as described in detail herein for the practice of my invention, except in this instance some or all of the pulp used contains sizing material as an integral part thereof. Of course in these cases additional sizing material may also be used, in which case this results in an enhancement of the sizing effect obtained. It is thus apparent that the use of pulps having sizing material as an integral part thereof falls within the scope of my invention.

In respect to the substantially water-soluble copper compound, I may use substantially water-soluble copper compound such as for example the sulphate, nitrate, chloride, or acetate, all of which are well known, as well as other well known substantially water-soluble copper compounds such as the chlorate, silicofluoride or the like, or double salts e. g. copper ammonium sulphate. Of course I may use water-insoluble or slightly water-soluble copper compounds such as copper hydroxide, oxide or carbonate, but in order to have it substantially effective, especially if it is substantially water-insoluble, I must treat the copper compound with an acidic material to produce a substantially water-soluble copper compound, and, in such cases, this is to be understood to be the equivalent of the substantially water-soluble copper compounds I employ. I can sometimes accomplish this by the use of a substantially water-insoluble copper compound, such as copper carbonate for example, which in certain instances when in contact with acidic material in the papermaking mix may produce a substantially water-soluble copper compound.

Also alkaline copper compounds e. g. copper-ammonia compounds may be used. Alkaline copper compounds may be used as such with good results, or their alkalinity may be reduced, if not completely neutralized, or the compound may even be acidified, with acidic materials. Or acidic material such as alum may be used in conjunction therewith if desired.

The substantially water soluble copper compounds are in the main cupric, nearly all of the cuprous compounds, at least those commercially available, being water insoluble or only very slightly soluble. However the cuprous compounds may be used if dissolved in a suitable solvent, such as an acid, but in such cases there is usually considerable oxidation to the cupric compound, so that the cuprous compound alone is not being used, but a mixture of the cuprous and cupric compounds. As most of the cuprous compounds tried do not appear to be as efficient as the cupric compounds, the cupric compounds are preferred.

My invention may be practiced if desired in connection with the treatment of alkaline filler with a substantially water-soluble copper compound, such as is described and claimed in my copending application Serial No. 679,994, filed July 11, 1933, now patent numbered 2,178,606, granted Nov. 7, 1939. In such case it is convenient to pretreat the alkaline filler, for example one derived from dolomitic material, with substantially water-soluble copper compound before adding to the papermaking mix, but this is not necessary. Although I do not restrict myself to the amount of substantially water-soluble copper compound used in such case, one percent on the weight of the alkaline filler is usually enough, but more or less may be used if desired. It will be noted in a discussion given previously herein, that when a substantially water-soluble copper compound is in the presence of alkaline filler before the copper compound has reacted with the size, the alkaline filler may also be acted upon by the copper compound without such pretreatment as is indicated above. As is well known in the art, the alkaline filler may be pretreated with an acidic material such as alum, and/or with a soap or oil emulsion or the like prior to addition to the paper mix, together with alum if desired, and such treatment of the alkaline filler may be employed in the practice of my invention, or as stated previously, the alkaline filler may be used untreated.

While it is convenient to use the size I employ, such as rosin size, in rather a dilute emulsion or solution such as for example one containing about 2% of rosin, I do not confine myself to the use of any definite concentration, but may use any concentration up to where the size is in thick paste form, or even in dry form.

It will be seen from the illustrative formulas given herein that I use in certain cases an amount of substantially water soluble copper compound, e. g. copper sulphate, calculated as $CuSO_4.5H_2O$, in weight equal to the weight (dry basis) of the sizing material, e. g. rosin size, employed, and in other cases equal to one and a half times the weight of the sizing material employed. It is to be understood, however, that I do not limit myself to these proportions but may vary them widely, and without being limited thereby I can state that for most purposes I employ a range from about one fifth to five parts of copper sulphate to one part by weight of rosin size, according to conditions, with the range of proportions shown in the illustrative formulas usually giving the optimum results.

As stated in the early part of this specification, I may use in the practice of my invention as little as $\frac{1}{10}$ of one percent of the substantially water-soluble copper compound (calculating the copper in the compound used to copper sulphate—$CuSO_4.5H_2O$—and basing the percentage on the weight of the fibre used). Thus where in the claims I employ the expression "copper compound," I means that there should be used not less than that much as a minimum in the processes claimed, and also in the processes from which resulted the products claimed.

The word "paper" is used herein in a broad sense to include products of all types, weights and thicknesses which contain fibrous material as a necessary constituent and which can be produced on a Fourdrinier, cylinder, or other forming, felting, or the like single or multi-ply paper or board machine. While in one of the illustrative formulas shown above I refer to the product as being suitable for book paper, it is to be understood that I am not in any way restricted to the manufacture of book paper, as the paper of my invention may be used for any of the variety of uses for which paper is used such as for printing paper of any kind including news, writing paper, wrapping paper, or the like, or for conversion, as to bags, coated paper, corrugated board, or in fact for any other use to which paper can be put which may possess as desired from only a slightly sized effect to complete waterproofing.

It is to be noted that in paper filled with alkaline filler wherein sizing material is employed, the use of a substantially water-soluble copper compound for reaction with the sizing material produces the unique, distinct, and wholly unex-

pected result of yielding a sizing effect, as tested by ink flotation, greatly superior to that obtained in either unfilled or clay filled paper, where only very poor sizing effect is obtained when such copper compound is employed for reaction with the sizing material.

This application is a continuation in part of my copending application Serial No. 679,994, filed July 11, 1933, now patent numbered 2,178,606, granted Nov. 7, 1939, and also a continuation in part of my copending application Serial No. 679,993, filed July 11, 1933, now patent numbered 2,186,040, granted Jan. 9, 1940, both of which as filed contained substantially identical disclosure in respect to the invention herein claimed, but which disclosure in application Ser. No. 679,993 has been cancelled because said disclosure and claims to different phases thereof are contained herein and in my copending application Ser. No. 679,994, now Patent No. 2,178,606.

While I have described in detail the preferred embodiments of my 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 my invention or the scope of the subjoined claims.

I claim:

1. Filled paper comprising fibrous material, a filler comprising alkaline earth metal carbonate, and the product derived from the bringing together of materials comprising rosin size and a substantially water-soluble copper salt in the presence of water.

2. Filled paper comprising fibrous material, a filler comprising calcium carbonate, and the product derived from the bringing together of materials comprising rosin size and a substantially water-soluble copper compound in the presence of water.

3. Filled paper comprising fibrous material, a filler comprising calcium carbonate, and the product derived from the bringing together of materials comprising rosin size and copper sulphate in the presence of water.

4. Filled paper comprising fibrous material, a filler comprising calcium carbonate, and copper resinate.

5. Filled paper comprising a filler which comprises calcium carbonate, and a substantially water-insoluble copper compound, said paper being derived from the bringing together of materials comprising fibrous material, a filler comprising calcium carbonate, rosin size, copper sulphate, and alum, in the presence of water.

6. The process for the manufacture of paper filled with a filler which comprises calcium carbonate, comprising mixing materials comprising fibrous material, a filler which comprises calcium carbonate, rosin size, and substantially water-soluble copper salt, and thereafter making paper therefrom.

7. The process for the manufacture of paper filled with a filler which comprises calcium carbonate, comprising mixing materials comprising fibrous material, a filler which comprises calcium carbonate, rosin size, a substantially water-soluble copper compound, and alum, and thereafter making paper therefrom.

8. The process of manufacturing paper filled with a filler which comprises calcium carbonate, comprising mixing material which comprise fibrous material, a filler comprising calcium carbonate, rosin size, and copper sulphate, and thereafter making paper therefrom.

9. The process of manufacturing paper filled with a filler which comprises calcium carbonate, comprising mixing materials which comprise fibrous material, a filler comprising calcium carbonate, rosin size, copper sulphate, and alum, and thereafter making paper therefrom.

10. In a process for the manufacture of paper filled with a filler comprising calcium carbonate, wherein materials are employed comprising fibrous material, a filler comprising calcium carbonate, and rosin size, the steps which consist in providing a substantially water-soluble copper compound and effecting a reaction between said copper compound and said size.

11. The process for the manufacture of paper filled with alkaline filler which comprises providing a wet paper web made from materials comprising fibrous material, a filler which comprises calcium carbonate, rosin size, and substantially water-soluble copper salt, and thereafter drying said web.

12. The process for the manufacture of paper filled with alkaline filler which comprises providing a wet paper web made from materials comprising fibrous material, a filler which comprises calcium carbonate, rosin size, substantially water-soluble copper salt, and alum, and thereafter drying said web.

13. Filled paper comprising fibrous material, alkaline filler in intimate association therewith, and a substantially water-insoluble copper compound resulting from the bringing together and interaction, in the presence of water, of a substantially water-soluble copper compound and a size selected from the group consisting of rosin sizes and fatty acid sizes.

14. Filled paper comprising a filler which comprises calcium carbonate, and a substantially water-insoluble copper compound, said paper being derived from the bringing together, in the presence of water, of materials comprising fibrous material, a filler which comprises calcium carbonate, a substantially water-soluble copper compound, and a size selected from the group consisting of rosin sizes and fatty acid sizes, said substantially water-insoluble copper compound resulting from the interaction of said substantially water-soluble copper compound and said size, said filler in said paper being in intimate association with said fibrous material.

15. Filled paper comprising a filler which comprises calcium carbonate, and a substantially water-insoluble copper compound, said paper being derived from the bringing together, in the presence of water, of materials comprising fibrous material, a filler which comprises calcium carbonate, a substantially water-soluble copper salt, acidic material, and a size selected from the group consisting of rosin sizes and fatty acid sizes, said substantially water-insoluble copper compound resulting from the interaction of said substantially water-soluble copper salt and said size.

16. Filled paper comprising a filler which comprises calcium carbonate, and a substantially water-insoluble copper compound, said paper being derived from the bringing together, in the presence of water, of materials comprising fibrous material, a filler which comprises calcium carbonate, a substantially water-soluble copper compound, alum, and a size selected from the group consisting of rosin sizes and fatty acid sizes, said substantially water-insoluble copper

compound resulting from the interaction of said substantially water-soluble copper compound and said size.

17. Filled paper comprising a filler which comprises calcium carbonate, and a substantially water-insoluble copper compound, said paper being derived from the bringing together, in the presence of water, of materials comprising a filler which comprises calcium carbonate, pulp having as an integral part thereof a size selected from the group consisting of rosin sizes and fatty acid sizes, and a substantially water-soluble copper compound, said substantially water-insoluble copper compound resulting from the interaction of said substantially water-soluble copper compound and said size.

18. The process for the manufacture of paper filled with alkaline filler, comprising mixing materials which comprise fibrous material, alkaline filler, a size selected from the group consisting of rosin sizes and fatty acid sizes, and a substantially water-soluble copper compound, and thereafter making paper therefrom, said size being reactive with said substantially water-soluble copper compound in the presence of water.

19. The process for the manufacture of paper filled with alkaline filler, comprising mixing materials which comprise fibrous material, alkaline filler, a size selected from the group consisting of rosin sizes and fatty acid sizes, a substantially water-soluble copper compound, and acidic material, and thereafter making paper therefrom, said size being reactive with said substantially water-soluble copper compound in the presence of water.

20. The process for the manufacture of paper filled with a filler which comprises alkaline earth metal carbonate, comprising mixing materials which comprise fibrous material, a filler comprising alkaline earth metal carbonate, a size selected from the group consisting of rosin sizes and fatty acid sizes, and copper sulphate, and thereafter making paper therefrom, said size being reactive with said copper sulphate in the presence of water.

21. The process for the manufacture of paper filled with a filler which comprises alkaline earth metal carbonate, comprising mixing materials which comprise fibrous material, a filler comprising alkaline earth metal carbonate, a size selected from the group consisting of rosin sizes and fatty acid sizes, a substantially water-soluble copper compound, and alum, and thereafter making paper therefrom, said size being reactive with said substantially water-soluble copper compound in the presence of water.

22. In a process for the manufacture of paper filled with alkaline filler wherein papermaking materials are employed comprising alkaline filler, fibrous material having sizing material as an integral part thereof, and a size selected from the group consisting of rosin sizes and fatty acid sizes, said size being reactive with a substantially water-soluble copper compound in the presence of water, the steps of introducing into said papermaking materials comprising said alkaline filler and said fibrous material and said size, a substantially water-soluble copper compound, and effecting a reaction between said copper compound and said size, thereby forming in the papermaking material a substantially water-insoluble copper compound having a sizing effect which is resistant to the deteriorating action of said alkaline filler in an aqueous medium.

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