

UNITED STATES PATENT OFFICE

2,140,394

METHOD OF PREPARING A STARCH ENVELOPED MINERAL MATERIAL

Harold T. Ruff, Chillicothe, Ohio, assignor to
The Mead Corporation, Chillicothe, Ohio, a
corporation of Ohio

No Drawing. Application January 25, 1934,
Serial No. 708,250

9 Claims. (Cl. 134—23)

This invention relates to the manufacture of paper, and more particularly to the manufacture of sized and unsized papers, of filled or coated character, such as are particularly useful as printing papers, or so-called book papers, and coated papers.

One of the principal objects of the invention is to provide a prepared starch-finely divided mineral material for use as a filler material, or in a coating color suspension, in the manufacture of paper.

Another object of the invention is to provide such a material for use in a rosin sized paper.

Still another object is to provide such enveloped filler or mineral material which is of predetermined controlled cluster size.

Another object of the invention is to provide a paper having such enveloped finely divided mineral material of controlled cluster size distributed in and/or upon the sheet, and the method of producing the same.

Another object of the invention is to provide such a paper which will be particularly free from "dusting" and "picking" on the printing machine and the method of producing such paper.

Another object of the invention is to provide a superior sized paper filled with a mineral material which is alkaline in reaction, and the method of producing the same.

Still another object is to provide a method, in the manufacture of paper, which comprises the preparation and utilization, of a starch sizing material, with mineral filler or coating material, which gives more economical and superior results in its utilization in the paper making process, and produces a paper of superior characteristics as to uniformity of cluster size and distribution of the filler material throughout the sheet, its comparative freedom from dusting and picking on the printing machine, its comparative freedom from odor and its superior color.

As is well known it has been a practice for many years to size paper to secure certain desired characteristics in the finished sheet. In some instances, the sizing material has been added to the fibrous furnish before it is fed on to the forming wire, so that the sizing is accomplished as a paper sheet is formed; while in other instances the formed sheet is sized, as for example in so-called "tub sizing" in which the formed sheet is passed through a bath of the size solution or suspension. A number of materials have been used for sizing, so-called rosin size being one of the best known. To some extent starch has also been used in sizing; but

in such cases, especially for printing papers, it has been found that an unduly large percentage of starch needs to be used to prevent dusting and picking of the papers upon printing, which of course has mitigated against such use because of the extra expense involved. Starch has been suggested to some extent as desirable to be used in connection with mineral filler material which is alkaline in reaction, such as calcium carbonate. Another difficulty has been experienced in the utilization of starch in filled papers in that there is ordinarily an uneven distribution of filler particles occasioned by the formation of filler clusters of uncontrolled character when flocculating agents are added to the sheets. These varying filler clusters produce a "wild" formation and result in non-uniformity, with variations in the degree of opacity and ink receptivity of different parts of the paper. Flocculation is ordinarily necessary with a starch size, when used as above referred to, to prevent such excess of the high losses of finely divided filler through the forming wire, and such flocculation to avoid the operating difficulties and expense results in the serious disadvantages in formation referred to.

In the manufacture of coated papers, casein is used almost universally as a binder or adhesive constituent of the suspension of finely divided mineral which forms the coating,—this suspension being normally referred to as a suspension of "coating color". Casein however is a comparatively expensive constituent of the paper. In addition casein as commercially available to the paper mill is not at all a uniform product and this occasions considerable difficulty in manufacture, as it is well known that very slight changes in constituent characteristics, concentrations, relative concentrations, etc. will produce marked variations in resulting products and that apparently insignificant changes in the paper making processes and constituents may cause such wide variations as make the difference between a commercially salable product and one which is not. Another objection to casein is that when once put into solution by means of suitable additive solvents, it cannot be kept for any considerable length of time but soon decomposes; and in addition it possesses an objectionable odor which makes paper containing it quite undesirable, if not entirely useless, for wrapping products, such as food products, the taste of which is materially affected by the casein odors. In addition casein solutions possess a dark yellowish brown color which must be offset

by the use of expensive fillers of unusually high white color where the final white color of the paper is of importance.

Despite these objectionable features casein has been used heretofore, at least for a number of years, to the practical exclusion of all other forms of sizing and adhesive materials in the preparation of so-called coated papers such as the coated papers which are used to such a large extent in the present day magazines for color picture reproduction. Starches have been generally considered substantially useless as an adhesive in making a coating color suspension.

By means of the present invention, however, starch can be used with completely satisfactory results as the adhesive material for a coating color suspension; and can also be used as an entirely satisfactory sizing material for either a filled or unfilled sheet, with hitherto unattained results.

In the practicing of this invention the starch is intimately admixed with the finely divided mineral material, in water, to produce an intimate and substantially homogeneous intermixture of the starch and mineral particles, and the suspension is then heated to a temperature sufficient to cause the starch granules to burst open while in this intimate and close juxtaposition to the mineral particles, and in so doing the bursting material released from the starch granules will intimately envelop the mineral particles contiguous to them, and the mineral particles will be intimately surrounded and wet by a starch film. The result is a suspension of the starch film surrounded mineral particles which will not be broken by the agitation to which it is subsequently subjected in the paper making sizing and coating processes.

As illustrative of a procedure which is satisfactory for the practicing of this invention, two parts of cold water may be added to one part of starch in a vessel preferably equipped with high speed stirring or other agitating device and provided with steam coils or other heating means suitable for heating up the water suspension of materials in the vessel. The slurry in the vessel is stirred and three to four parts of finely divided mineral filler material are added during the stirring, and until the mineral material and the starch slurry are intimately and thoroughly admixed. The mixture is then heated until the starch granules burst and on so doing the starch material within the granules will intimately envelop the mineral filler particles contiguous to them and surround the several particles with a wet starch film. Very satisfactory results will be secured if the mixture or suspension is heated to 185° F., by means of steam coils, and maintained at that temperature while being agitated for about fifteen minutes. During this heating and agitation the starch granules will burst and the resulting wet film coating of the mineral particles will result. The material within the vessel is then allowed to cool and jelly. The jelly can then be broken, as by means of a high speed stirrer or other suitable devices and its viscosity thus reduced without destroying the homogeneous distribution of the filler particles, within their several starch films, throughout the mass. Also, the jelly having been broken the mass can be diluted to any degree desired without appreciably affecting the condition of the mineral-starch film particles. From experience in practicing this invention the mass can be diluted almost infinitely without causing any apparent variation in the condition of the

particles, and certainly it can be diluted at will within any range of dilution needed for utilization in the paper making and coating process.

In addition to breaking the jelly down by means of stirrers, the same result can be accomplished by centrifugal pumping of the jelled mass, or by grinding it in a pebble mill, or the like.

The starch filmed mineral particles are present in an extremely fine state of subdivision, and are held in that condition, and in a state of extremely uniform distribution. And when added to a paper forming stock or furnish will maintain that uniform distribution and produce an unusually uniform distribution of filler throughout the paper sheet. Where an extreme state of subdivision, such as can be secured under this invention, is detrimental because of the resulting filler losses when a comparatively large proportion of the filler suspension material is carried through the screen into the effluent system, this difficulty can be readily overcome by the addition of suitable amounts of flocculating agent. The flocculating agent can be added in desired or controlled amounts to give desired or controlled degree of flocculation, and the resulting flocculation will produce substantially uniform results in building up the finely divided filler-starch filmed particles into clusters or sizes which will also be of quite uniform character. As a result the size of the clusters thus formed may be readily controlled over a wide range, from practically colloidal size up to quite coarse, readily settling aggregates or clusters.

The material thus prepared is not only usable for making filled paper but is especially adaptable for use as a coating color suspension for making coated paper, such as the coated book paper referred to above. Also, of course, the relative percentage of starch and mineral material, produced, may be varied to give the desired characteristics to the paper in which it is used. The character of the starch used has some appreciable effect, root starches such as tapioca and potato starch giving better sizing effects than do the cereal starches. The material as thus prepared has most extraordinary characteristics when compared with mixtures of mineral material and starch as prepared in other ways, or when compared with boiled starch alone. When mineral filler material is added to boiled starch in quantities large enough to give the necessary color and opacity, it has been found that either a thick viscous paste results, so thick that it will not permit of proper flow or of proper application and spreading on the paper by usual devices such as are used in applying coating color to paper, or a flocculation of the mineral material will occur entirely defeating the desired purpose of use of the starch as a binding agent. Where a thin mixture was used with a view to avoiding the above difficulties opacity suffered quite materially, and whatever resultant coat remained upon the paper as a coat adhered but poorly, and in the case of filler the filler particles were bound very poorly to the paper, with the result that what is known as "dusting" and "picking" were present to an inordinately large degree.

It is not definitely understood just why starch-mineral suspension prepared as above described has these very extraordinary and unusual characteristics. In fact, there is little if any definite information as to the nature of a starch jelly, and as to what changes take place when a jelly is formed and when it is broken down. Furthermore the structure of jells in general is a con-

controversial one in science; but despite this lack of accurate information from the purely scientific point of view, it has been found that when the starch granules are caused to burst when thus intimately admixed with the finely divided mineral particles the result is to produce the mineral particle-starch film product which has the unusual and extraordinary characteristics herein referred to.

As an example of processing to produce a coating color suspension, satisfactory results have been secured with the following relative proportions and procedure,—120 grams of tapioca starch is first mixed cold with 200 ml. of water. This cold suspension is then mixed with 400 grams of finely divided mineral material, such as calcium carbonate, in 1300 ml. of water. The mixture is then heated to 90° centigrade and kept at that temperature for about thirty minutes. It should then be ground in a suitable way, as in a rod mill or pebble mill for about twenty minutes. This will give a fluid coating color suspension which has little or no tendency to jell on standing. Aging this coating color at room temperatures for twenty hours or even more will further improve the sizing or adhesive characters thereof. While alkaline material has found quite limited use heretofore in the paper industry, its usage having been confined so far as applicant is aware to only one or two companies, up until quite recently, applicant's own experience in connection with the use of such an alkaline filler material as is made from causticizing high magnesium lime, over a long period, has shown there are difficulties incident to the use of such an alkaline material in a paper where one or more of the ingredients which go to make up the paper in its manufacture are acid in character and therefore of such character as to react with the alkaline material such as calcium carbonate. A filler-starch film material of the character produced by this invention completely avoids these difficulties which have heretofore been attendant upon the use of alkaline filler materials as the material produced according to this invention, in any dilutions and under any conditions of use which have thus far been encountered, is of such character that the objectionable reaction between the acid materials, such as alum and the alkaline mineral material is avoided. As a result the control of time of contact as between the acid and alkaline material which has heretofore been exercised in the commercial operations with which applicant is associated is entirely unnecessary. In fact, whereas it has been the usual practice to introduce the alum at the riffles, and just before the diluted stock-filler suspension goes on to the forming wire, in order to cut down the reaction period, with filler-starch suspensions made according to this invention all of the ingredients can be introduced into the beater and the question of time is of no operating consequence. Not only that but through the introduction of the alum into the beaters flocculation is more definitely controlled and consequently losses through the wire into the effluent system are decreased.

In the making of a coating color suspension good results can be secured with the following relative proportions and procedure,—100 grams of dry alkaline filler and 200 ml. of water are mixed with a suspension of 15 grams of tapioca flour starch in 50 ml. of water. This suspension is then heated to 90° centigrade and maintained

at that temperature for some fifteen to twenty minutes. The jell is then thinned by suitable mechanical processing and water added to give a suspension of the proper viscosity and containing the desired amount of solids. When diluted to viscosity approximating that of the ordinary coating color suspension containing casein and the usual amount of solids, the resulting color contains approximately 28% of solids. Such a color suspension when applied to the paper and supercalendered gave unusually fine results on the standard "pick" test. As an alternative the mineral-starch film suspension after being thinned by suitable mechanical processes may have added to it 5 grams of casein dissolved in 25 ml. of water containing 6 grams of Na_2CO_3 .

As an illustration of procedure in manufacturing book paper of very low sizing content, the following procedure has been found satisfactory,—a suitable amount of alkaline filler (depending on the amount of filler desired to be contained in the finished paper sheet) is cooked with 10% starch at a suitable temperature, the cooked mixture being circulated through a centrifugal pump to prevent jelling. It has been found that a temperature of 80° C. is usually adequate for causing rupture of the starch granules; but temperature in excess of that may be used. 450 pounds of dry weight of this material is added to a 3000 pound beater. Alkaline filler can be added at the beater if desired; or no additional alkaline filler need be added except what is added in the form of broke, and the balance of filler for the sheet may be added to the wire side of the sheet during the formation thereof, as set out in U. S. Patent to William Edison Bair No. 1,875,208 which belongs to the assignee of the present application. An amount of alum desired to give the necessary flocculating effect, and to thus control the amount passing through the wire into the effluent system, may be added in the riffles. Where a carbonate filler is used the alum can still be added in the beater in such proportion as desired. Increasing the percent of alum, with the proportions above referred to, from 1 to 2% would result in such coarser agglomerates of the filler-starch film particles as to cut down the effluent losses in half. The agglomerates so produced while coarser are of cluster sizes substantially uniform, so far as practical results are concerned, and are uniformly distributed in the sheet. And as the size of the agglomerates or clusters may be controlled at will by the addition of alum or other flocculating agent, a sheet may be formed containing the filler material from very fine, almost colloidal size, particles to comparatively quite large clusters.

As an illustration of a rosin sized paper, such as a book paper, manufactured through the utilization of the present invention the following proportions and procedure are satisfactory,—to a paper furnish containing approximately 50% soda and 50% sulfite pulps, 2% rosin size and 4% alum were added in the beater in the usual manner. After the sizing reaction was completed in the beater, the desired additional quantity of filler-starch film suspension was added. A satisfactory filler starch suspension to be used is the one made from alkaline material as set out immediately above. This was mixed for a short time and the beater dropped. All of the alum can be added in the beater or if desired additional alum can be added before delivery to the machine.

As compared with the efforts at starch sizing, as heretofore practiced, such as in so-called soft sized sheets, the sizing can be effected by the practicing of the present invention with very large savings in the amount of starch,—from 33 to 50% less than when the starch is boiled separately and then added to the filler as in such instances of use of starch as have heretofore been practiced. And a lower viscosity mixture is obtained by the practicing of the present invention than can be obtained by adding the equivalent in sizing of separately boiled starch. Furthermore, when diluted to very low consistencies,—for example to 5% of solids—, the suspension of the present invention does not flocculate and settle nearly as readily as a suspension made with starch boiled separately. The mineral-starch film suspension gives a water suspension which is unusually slow settling compared with filler in suspension alone. A starch alkaline material as prepared according to this invention may be mixed directly with a solution of casein; and may be sized with rosin and alum with practically no loss in sizing efficiency or excessive use of alum. Also paraffin may be incorporated in these suspensions to improve the finish of the paper, and to impart increased ink resistance.

While the method and product herein described constitute preferred embodiments of the invention, it is to be understood that the invention is not limited to this precise method and product, and that changes may be made therein without departing from the scope of the invention which is defined in the appended claims.

What is claimed is:

1. The method of preparing a starch enveloped mineral material for use as a filler or coating material or the like in the manufacture of paper which consists in mixing starch granules into water to form a starch granule slurry, adding finely divided mineral material to said starch slurry, stirring the starch slurry and added mineral material to distribute the mineral particles throughout the slurry and effect intimate admixture of the particles and the starch granules in the slurry, heating said intimate admixture to cause bursting of the starch granules and liberation of the starch contents thereof immediately adjacent the mineral particles whereby to cause such liberated starch material in the slurry to form upon the mineral particles an enveloping and protecting film and to effect a suspension of such starch film enveloped particles, cooling such suspension to cause it to jell, and breaking down such jell by agitation to form a homogeneous, flowable suspension of such film enveloped mineral particles and without destroying said film enveloped condition.

2. The method of preparing a starch enveloped mineral material for use as a filler or coating material or the like in the manufacture of paper which consists in mixing starch granules into water to form a slurry, adding approximately two parts water and one part of root starch, adding three to four parts of finely divided mineral material to the slurry, stirring the starch slurry and added mineral material to distribute the mineral particles throughout the slurry and effect intimate admixture of the particles and the starch granules in the slurry, cooking said intimate admixture 80–90° C. to cause bursting of the starch granules and liberation of the starch contents thereof immediately adjacent the mineral particles whereby to cause such liberated starch material

in the water to form upon the mineral particles an enveloping and protecting film and to effect a suspension of such starch film enveloped particles.

3. The method of preparing a starch enveloped mineral material for use as a filler or coating material or the like in the manufacture of paper which consists in mixing starch granules into water to form a starch granule slurry, adding finely divided mineral material to said starch slurry, stirring the starch slurry and added mineral material to distribute the mineral particles throughout the slurry and effect intimate admixture of the particles and the starch granules in the slurry, heating said intimate admixture to cause bursting of the starch granules and liberation of the starch contents thereof immediately adjacent the mineral particles whereby to cause such liberated starch material in the slurry to form upon the mineral particles an enveloping and protecting film and to effect a suspension of such finely divided starch film enveloped particles.

4. In the manufacture of paper, the method of preparing a starch enveloped mineral material for use as a filler or coating material or the like in the manufacture of paper which consists in mixing starch granules with water and agitating to form a starch granule slurry, adding finely divided mineral material to said starch slurry while agitating and continuing the agitation to distribute the mineral particles throughout the slurry and effect intimate admixture of the particles and the starch granules in the slurry, heating said intimate admixture to cause bursting of the starch granules and liberation of the starch contents thereof immediately adjacent the mineral particles whereby to cause such liberated starch material in the water to form upon and about the mineral particles an enveloping and protecting film and to effect a suspension of such starch film enveloped particles.

5. The method of preparing a starch enveloped mineral material for use as a filler or coating material or the like in the manufacture of paper which consists in mixing starch granules into water to form a slurry, adding finely divided mineral material to said starch granule slurry, stirring the starch slurry and added mineral material to distribute the mineral particles throughout the slurry and effect intimate admixture of the particles and the starch granules in the slurry, heating said intimate admixture to cause bursting of the starch granules and liberation of the starch contents thereof immediately adjacent the mineral particles whereby to cause such liberated starch material to form upon the mineral particles an enveloping and protecting film and to effect a suspension of such starch film enveloped particles, cooling such suspension to cause it to jell, breaking down such jell by high speed agitation to form a homogeneous, flowable suspension of such film enveloped mineral particles and without destroying said film enveloped condition, and diluting such flowable suspension of film enveloped particles for use as a filler material or the like in paper making.

6. The method of preparing a starch enveloped mineral material for use as a filler or coating material or the like in the manufacture of paper which consists in mixing starch granules into water to form a slurry, adding finely divided carbonate mineral material to said starch granule slurry, stirring the starch slurry and added mineral material to distribute the mineral

particles throughout the slurry and effect intimate admixture of the particles and the starch granules in the slurry, heating said intimate admixture to cause bursting of the starch granules and liberation of the starch contents thereof immediately adjacent the mineral particles whereby to cause such liberated starch material in the slurry to form upon the mineral particles an enveloping and protecting film and to effect a suspension of such starch film enveloped particles.

7. The method of preparing a starch enveloped mineral material for use as a filler or coating material or the like in the manufacture of paper which consists in mixing starch granules into water to form a slurry, adding finely divided carbonate mineral material to said starch granule slurry, stirring the starch slurry and added mineral material to distribute the mineral particles throughout the slurry and effect intimate admixture of the particles and the starch granules in the slurry, heating said intimate admixture to cause bursting of the starch granules and liberation of the starch contents thereof immediately adjacent the mineral particles whereby to cause such liberated starch material to form upon and about the mineral particles an enveloping and protecting film and to effect a suspension of such starch film enveloped particles, cooling such suspension to cause it to jell, and breaking down such jell by high speed agitation to form a homogeneous, flowable suspension of such film enveloped mineral particles and without destroying said film enveloped condition.

8. The method of preparing a starch enveloped mineral material for use as a filler or coating material or the like in the manufacture of paper which consists in mixing approximately one part of starch granules into two parts of water to form a starch granule slurry, adding three to four parts of finely divided mineral material to said starch slurry, stirring the starch slurry and added mineral material to distribute the mineral particles throughout the slurry and effect intimate ad-

mixture of the particles and the starch granules in the slurry, heating said intimate admixture to a temperature of substantially 80-90° C. to cause bursting of the starch granules and liberation of the starch contents thereof immediately adjacent the mineral particles whereby to cause such liberated starch material in the slurry to form upon the mineral particles an enveloping and protecting film and to effect a suspension of such starch film enveloped particles, cooling such suspension to cause it to jell, and breaking down such jell by high speed agitation to form a homogeneous, flowable suspension of such film enveloped mineral particles and without destroying said film enveloped condition.

9. The method of preparing a starch enveloped mineral material for use as a filler or coating material or the like in the manufacture of paper which consists in mixing starch granules into water to form a slurry, adding finely divided mineral material to said starch granule slurry, stirring the starch slurry and added mineral material to distribute the mineral particles throughout the slurry and effect intimate admixture of the particles and the starch granules in the slurry, heating said intimate admixture to cause bursting of the starch granules and liberation of the starch contents thereof immediately adjacent the mineral particles whereby to cause such liberated starch material to form upon the mineral particles an enveloping and protecting film and to effect a suspension of such starch film enveloped particles, cooling said suspension to cause it to jell, breaking down such jell by high speed agitation to form a homogeneous, flowable suspension of such film enveloped mineral particles and without destroying said film enveloped condition, diluting such flowable suspension of film enveloped particles for use as a filler material or the like in paper making, and adding a flocculating material to the diluted flowable suspension to cause agglomeration of said film enveloped mineral particles into clusters.

HAROLD T. RUFF.