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CLAY PRODUCT AND PROCESS OF
PREPARING SAMEWilliam T. Maloney, Natural Bridge, N. Y., as-
signor to Georgia Kaolin Company, a corpora-
tion of GeorgiaNo Drawing. Application November 26, 1934,
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12 Claims. (Cl. 91—68)

My invention relates to an improved clay and method of making it, and also to a paper coated therewith.

One of the objects of my invention is to produce a clay the particles of which are in such a state as to render the clay particularly desirable for use in coating paper, and, more particularly, an object of my invention is to produce a clay, a substantial portion of the particles of which have a certain size range.

Another object of my invention is to separate the particles of clay of the desired size, and more particularly to effect this separation by processes such as dispersion or deflocculation, and if necessary to break up agglomerates of clay particles by processes such as grinding.

A further object of my invention consists in producing a fibrous material, such as paper, coated with my improved clay admixed with a suitable binder, such as starch or casein. Another object of my invention is to reduce the amount of binder required.

A further object of my invention consists in producing a clay coated paper with a high finish and a high quality from the viewpoint of color, i. e., white.

Another object of my invention is to produce a substitute for satin white and a paper coated with this material, whereby the clay coated paper will approximate in its finish qualities a paper coated with satin white.

Further objects of my invention will become apparent as the description of it proceeds.

In the prior art it has been known to coat paper with mineral materials such as clays, satin white, calcium carbonate, etc., admixed with suitable binders, such as starch, casein, glue, etc. The mineral material may be applied to the paper by any of a number of known mechanical procedures. It may be applied near the conclusion of the paper-making operation, before the paper web is completely dry, or it may be applied after the paper is finished and dried. This coating produces a smooth surface on the paper which is desirable in certain printing operations, particularly half-tone printing.

Paper is distinguished by its color and finish. The finish is independent of the color, for example, a paper may have a good color and a poor finish and vice versa. The finish is readily apparent to a person skilled in the art but its accurate determination is made by an instrument known in the art as a glarimeter.

Ordinarily when a high quality paper has been desired, with a high finish, it has been the more

or less general practice to employ satin white as an ingredient of the coating composition. Satin white is, however, an artificially made material and relatively expensive. Moreover, satin white requires a relatively large amount of binder as compared with the amount required when clay is used. For these reasons, it is less economical to use than clay and other materials and the papers so coated have been relatively expensive to make. Papers coated with the clays heretofore available have been regarded as inferior in finish and color to those coated with satin white.

I have discovered a process of treating clay whereby the resulting improved product may be used as a substitute for satin white and when used in a coating will produce a paper of a finish quality approximating that obtainable by using satin white.

More particularly, I have discovered that one of the factors which contributes to the finish and color of a clay coated paper is the size of the clay particles, and that if the clay is treated so that a large percentage of clay particles have a size range between .1 and 2 microns, a paper coated with a mixture of this clay product and a suitable binder is superior in color and finish to paper heretofore produced by coating with clay, and approximates in finish results the paper obtainable by the use of satin white.

In producing my clay product it is very desirable that there should not be too great a proportion of particles of colloidal size because material of this fineness has little hiding power or opacity and, therefore, detracts from the color. On the other hand there should not be a large amount of particles over 2 microns in size. In carrying out my invention, therefore, I aim to produce a clay in which a very large percentage of the particles are under 2 microns in size and yet does not contain too great a proportion of colloidal material.

In the prior art it has been recognized that minerals used for coating paper should consist of particles of a small size and that the presence of too large size particles in the mineral, for example, .001" or greater, would produce spots in the sheet and cause other undesirable characteristics in the paper. However, when clays are treated to remove only this coarse grit, a paper results which is not markedly superior in color or finish to that obtainable in ordinary clay coated papers, as has been known for some time.

I am not aware, however, of any disclosure that the particular size range corresponding to the particles in my clay product is advantageous,

and it is wholly unobvious from any prior art with which I am familiar that my particular clay product should produce a paper having the superior properties recited. Nor has there been any teaching how this clay may be produced. So far as I am aware, none of the processes of the prior art will produce a clay coated paper with properties comparable with those possessed by my paper.

My novel clay product may be produced by various procedures. However, these procedures all include, as essential steps, first bringing the clay into a dispersed or deflocculated state in an aqueous suspension, and then, while the clay is in the highly dispersed state in the water suspension, subjecting it to a separating treatment to effect separation of the coarser particles above the predetermined size range from the suspension, leaving the finer particles of the desired size range in suspension in the water medium. This finer fraction is then recovered in a suitable state for use in a paper coating composition. For the purpose of increasing the yield of the desired fine particle fraction, it is sometimes advantageous to subject the clay to a preliminary grinding treatment. The exact details of the process will depend upon the nature of the clay available as the raw material, as I will point out later. For example, if the clay already contains a large percentage of particles under 2 microns in size, as much grinding may not be necessary as if the clay consisted primarily of larger particles.

Clays suitable for use in paper making may be employed. In general it may be stated that it is better to use a soft clay. A soft clay is one in which the lumps can be rubbed out after the clay has become wet and then dried.

If a soft clay occurs by itself in the deposit it may be taken out separately and treated. If hard and soft clays occur together, they may be air separated and the soft clay treated. The size of the original clay agglomerates is not so important except as it may affect the yield of particles of the required size and the time required for grinding, if grinding is employed as a step in the process. The clays I have found particularly desirable include Georgia clays such as Sandersville and Dry Branch clays.

In some instances the clay may be subjected to my process just as it comes from the deposit. If the clay is wet, however, as it occurs in the deposit, (containing over 5% natural moisture) I find it desirable to first dry the clay to eliminate the moisture down to at most 5%. This is preferably effected by air drying and aging, but if weather conditions do not permit, then the clay may be subjected to artificial drying. I have found that a naturally occurring wet clay, while it may be soft and of an advantageous particle size, does not respond as rapidly to my treatment as does a dry clay. For example, an English clay which is a soft wet clay is not improved a great deal by grinding alone. If it is first dried, the improvement upon being subjected to my process is remarkable.

In carrying out that form of my process in which the clay is subjected to grinding, I place a suitable clay in a pebble mill and add to it water and a deflocculating or dispersing agent. The proportions of clay, water and dispersing agent may vary but I find that a mixture of from 50 to 75% clay gives desirable results. The deflocculating agents are preferably potassium hydroxide and sodium silicate; the latter is preferred because it is relatively inexpensive and works very

satisfactorily. Others may be used, such as potassium hydroxide and casein, calcium hydroxide and casein, ammonia and casein or dextrin or dextrin gums in admixture with ammonia or potash. The amount of dispersing agent varies between 2000 cc. and 6000 cc. 40° Bé. sodium silicate to the ton of clay, depending on the time of grinding. If the time of grinding is relatively short, a smaller amount of dispersing agent will be needed than if a longer grinding period is employed. I find it desirable to employ a minimum amount of the dispersing agent for the reason that too great an excess, while not affecting the color or size of the particles, tends to produce a less desirable finish.

This mixture is then ground and at the conclusion of the grinding, the slip produced is drawn off, diluted with water, and the coarser clay settled or separated by centrifuging. The object of the grinding is to produce a high yield of clay, preferably 60% or more consisting of particles of a size of 2 microns or smaller, but containing as little true colloidal clay as possible. In practice the percentage may vary somewhat on each side of this figure depending on the clay used and will be smaller if a shorter grinding time is employed. The amount of grinding will depend somewhat on the properties of the clay and the economics involved. In general it is not economical to grind over three hours, as the increase in particles of the desired size is out of proportion to the power consumed, and too many particles of colloidal size may be produced. Any grinding conditions which will fulfill these requirements are within the scope of my invention, but I have found that a pebble mill, preferably with small pebbles, is desirable. The dilution, after grinding and preliminary to separation of the fine fraction, may vary over wide limits but in general I dilute the mixture to about 25% solids. In effecting the separation of the fine fraction, the coarser particles may be allowed to settle in a tank settler and part or all of the grit is thus settled out. This settling may be continued until all of the coarse clay settles, or after a preliminary settling, the remainder of the coarse clay may be separated by centrifuging, for example, in a Laughlin continuous type centrifuge.

In the prior art, it has been quite common to dilute the slip to a larger extent than I have specified, i. e., 3% to 20% clay. I have discovered that by using the higher clay mixture the separation of the coarse particles may be obtained more quickly when they are separated by settling and that in case a centrifuge is employed the mixture has the right consistency for the centrifuging operation.

It is not absolutely necessary to have the dispersing or deflocculating agent in the mixture during the grinding. It should be present, however, in the classifying step to promote the separation of the coarse and fine particles. For example, I can grind the clay without dispersing, then disperse and dilute, or dilute and then disperse, and classify. However, by using the dispersing agent during the grinding, the clay has a greater fluidity and this aids in the roll of the pebbles. It also permits the use of a higher percentage of clay in the grinding mixture.

The proportion of clay of the desired size range remaining in suspension after the settling or centrifuging will vary from 40% to 60% of the amount of the raw material used depending on the clay used, and the time of grinding (when grinding is employed). This portion will com-

prise particles at least about 80 to 90% of which are of a size less than 2 microns and yet a small portion of which is of colloidal size.

This suspended clay is then flocculated, for example, by the addition of lime or alum. The clay then may be filtered and dried if desired.

If the clay has a sufficiently large percentage of fine particles, and other desirable characteristics, the grinding may be dispensed with. The particles of the desired size may be separated by dispersing with a deflocculating agent and settling or centrifuging or both. The use of the centrifuge in the separating is optional. It is desirable, however, in any of the variations of my process because it speeds up the separation and results in a more accurate classification. I have found, however, that grinding is one of the factors which improves the color of the clay coated paper. I wish it to be understood, however, that my invention is not limited to a process in which the clay is ground.

According to a specific example, which is recited merely as illustrative of the general process embodying my invention, one ton of Sandersville clay (dry) is placed in a pebble mill with 1000 lbs. of water and 2000 cc. of 40° Bé. sodium silicate. The mill is operated for about one hour and the slip produced is drawn off and diluted with 240 gallons of water and centrifuged using a Laughlin type continuous centrifuge. Under these conditions a fine fraction consisting of clay particles within the desired size range and amounting to about 40% of the amount of clay will be obtained. The coarse clay is continuously removed and may be returned to the pebble mill for further grinding or utilized as a less desirable grade of clay. The clay of the desired size range remains suspended in the water and flows out of the centrifuge. This is flocculated by the addition of alum or any other flocculating agent and filtered. The clay may then be dried.

The procedure above described may be modified by employing 6000 cc. of 40° Bé. sodium silicate and by running the pebble mill for three hours.

I may also employ Macon (Georgia) clay and subject it to the procedure recited in either of the preceding paragraphs.

After my improved clay is produced by the above described process it is mixed with a binder and applied to paper by methods well known in the paper coating art. Any of the conventional binders may be used. I have found, however, that casein is very desirable.

With my clay substitute for satin white I am able to use a much smaller amount of casein than is required when satin white is used and in some instances amounts as low as 15% will suffice. In producing a hard size with a waterproofing effect, casein in an amount not over 20% may be employed. This results in a double saving because my improved clay is cheaper than satin white and the amount of casein needed is less.

While processes of coating paper with clay employing amounts of casein comparable to that I am enabled to employ are known, such processes apply to ordinary clay in which the particles are of larger size than in my process and the resulting coated paper is inferior from the standpoint of finish and color to that obtainable by my process.

Where I use the words "coating" or "coated" herein, I refer to the application of the material to the surface of the paper in any manner and at any time subsequent to the formation of the paper pulp into a web, either before or after it has dried.

By "colloidal" I refer to particles of a size smaller than .1 micron.

By my process there is produced a finely divided mineral material adapted for use in place of satin white and consisting of a fine fraction of clay containing colloidal and non-colloidal smaller particles of such size and in such proportions as to impart desirable surface characteristics of gloss and color when applied to paper.

While I have described in detail advantageous embodiments of my invention, it is to be understood that my invention may be varied considerably within the limitations required by the disclosures in the prior art without departing from the spirit of my invention or the scope of the following claims.

I claim:

1. The process of treating Georgia clay to provide a finely divided material adapted for use in coating paper which comprises mixing the clay with water to form a diluted aqueous suspension, introducing a dispersing medium to said suspension to increase the dispersion of the clay, subjecting said suspension to a controlled centrifuging to effect a separation of the clay into a finer suspended fraction containing colloidal and non-colloidal smaller particles of such size and in such proportions as to impart desirable surface characteristics of gloss and color when applied to paper and into a fraction containing larger particles, adding a flocculating agent to the suspended fraction, and filtering the flocculated fraction to provide a finely divided mineral material adapted for use in place of satin white.

2. The process of treating clay to provide a finely divided material adapted for use in coating paper which comprises mixing the clay with water to form a diluted aqueous suspension, introducing a dispersing medium to said suspension to increase the dispersion of the clay, subjecting said suspension to a precipitating force under controlled conditions to effect a separation of the clay into a finer suspended fraction containing colloidal and non-colloidal smaller particles of such size and in such proportions as to impart desirable surface characteristics of gloss and color when applied to paper and into a fraction containing larger particles, adding a flocculating agent to the suspended fraction, and filtering the flocculated fraction to provide a finely divided mineral material adapted for use in place of satin white.

3. The process of treating clay to provide a finely divided material adapted for use in coating paper which comprises mixing the clay with water and with a dispersing agent and bringing the clay into a deflocculated state in an aqueous suspension, subjecting said suspension to a controlled precipitating treatment to effect a separation of the clay into a finer suspended fraction containing colloidal and non-colloidal smaller particles of such size and in such proportions as to impart finish characteristics when applied to paper substantially equal to those obtainable with satin white and into a fraction containing larger particles, and recovering the finer fraction from the suspension.

4. The process of treating clay to provide a finely divided material adapted for use in place of satin white in coating paper which comprises mixing the clay with water and with a dispersing agent and bringing the clay into a deflocculated state in an aqueous suspension, subjecting said suspension to a precipitating force under controlled conditions to effect a separation of the clay into a finer suspended fraction containing

colloidal and non-colloidal smaller particles of such size and in such proportions as to impart desirable finish characteristics when applied to paper substantially equal to those obtainable with satin white and into a fraction containing larger particles, adding a flocculating agent to the suspended fraction, and filtering the flocculated fraction to provide a finely divided mineral material adapted for use in place of satin white.

5. The process of treating clay to provide a finely divided material adapted for use in place of satin white in coating paper which comprises mixing the clay with water and with a dispersing agent and bringing the clay into a deflocculated state in an aqueous suspension, subjecting said suspension to a precipitating force under controlled conditions to effect a separation of the clay into a finer suspended fraction containing colloidal particles and non-colloidal smaller particles at least about 80% of which are of a size between 0.1 and 2 microns and adapted to impart desirable surface characteristics of gloss and color when applied to paper and into a fraction containing larger particles, and recovering the finer fraction from the suspension.

6. The process of treating clay to provide a finely divided material adapted for use in coating paper which comprises mixing the clay with water and with a dispersing agent and bringing the clay into a deflocculated state in an aqueous suspension, subjecting said suspension to a controlled centrifuging to effect a separation of the clay into a finer suspended fraction containing colloidal and non-colloidal smaller particles at least about 90% of which are of a size two microns and smaller and in such proportions as to impart desirable surface characteristics of gloss and color when applied to paper and into a fraction containing larger particles, adding a flocculating agent to the suspended fraction, filtering said suspended fraction and recovering the flocculated fine fraction as a finely divided mineral material adapted for use in coating paper.

7. The process of treating clay to provide a finely divided material adapted for use in coating paper which comprises grinding the clay with water in the presence of a dispersing agent and bringing the clay into a deflocculated state in aqueous suspension, subjecting said suspension to a precipitating force under controlled conditions to effect a separation of the clay into a finer suspended fraction containing colloidal and non-colloidal smaller particles of such size and in such proportions as to impart desirable finish characteristics when applied to paper substantially equal to those obtainable with satin white and into a fraction containing larger particles, and recovering the finer fraction from the suspension.

8. The process of treating clay to provide a finely divided material adapted for use in place of satin white in coating paper which comprises mixing the clay with water and a dispersing agent and bringing the clay into a deflocculated state in an aqueous suspension consisting of about 25% or more clay solids, subjecting said suspension to a precipitating force under controlled conditions to effect a separation of the clay into a finer suspended fraction containing colloidal and non-colloidal smaller particles of such size and in such proportions as to impart desirable finish characteristics when applied to paper substantially equal to those obtainable with satin white and into a fraction containing larger particles, and recovering the finer fraction from the suspension.

9. As a product of manufacture, a finely divided material adapted for use in place of satin white in paper-coating compositions, consisting of a clay fraction produced from clay by successively bringing the clay into a deflocculated state in an aqueous suspension, subjecting said suspension to a precipitating force under controlled conditions to effect a separation from said suspension of particles above a predetermined size range, and then recovering the smaller particles remaining in suspension, said clay fraction comprising the particles recovered from said suspension and consisting of colloidal and non-colloidal smaller particles of which at least about 80% are between 0.1 and 2 microns, inclusive, in size, and in such proportions as to impart desirable surface characteristics of gloss and color when used in coating paper.

10. As a product of manufacture, a finely divided material adapted for use in place of satin white in paper-coating compositions, consisting of a clay fraction produced from clay by successively bringing the clay into a deflocculated state in an aqueous suspension, subjecting said suspension to a precipitating force under controlled conditions to effect a separation from said suspension of particles above a predetermined size range, and then recovering the smaller particles remaining in suspension, said clay fraction comprising the particles recovered from said suspension and consisting of colloidal and non-colloidal smaller particles at least 90% of which are of a size two microns and smaller and in such proportions as to impart desirable surface characteristics of gloss and color when used in coating paper.

11. A paper product particularly adapted for use in half-tone printing and for similar purposes, having a surface formed by a coating containing a finely divided mineral material consisting of a fine clay fraction substantially identical with that produced by successively bringing the clay into a deflocculated state in an aqueous suspension, subjecting said suspension to a precipitating force under controlled conditions to effect a separation from said suspension of particles above a predetermined size range, and then recovering the smaller particles remaining in suspension, and consisting of colloidal particles and non-colloidal smaller particles, of which at least 80% are between 0.1 and 2 microns, inclusive, in size, and in such proportions as to impart desirable finish characteristics when applied to paper substantially equal to those obtainable with satin white.

12. A paper product particularly adapted for use in half-tone printing and for similar purposes, having a surface formed by a coating containing a finely divided mineral material consisting of a fine clay fraction substantially identical with that produced by successively bringing the clay into a deflocculated state in an aqueous suspension, subjecting said suspension to a precipitating force under controlled conditions to effect a separation from said suspension of particles above a predetermined size range, and then recovering the smaller particles remaining in suspension, and consisting of colloidal particles and non-colloidal smaller particles at least 90% of which are of a size two microns and smaller, and in such proportions as to impart desirable finish characteristics when applied to paper substantially equal to those obtainable with satin white.