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PROCESS OF DRUM-FINISHING COATED PAPER AND PRODUCT

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This invention relates to the manufacture of drum-finished mineral-coated paper, including coating compositions used and the coated paper product made therewith.

Drum-finished mineral-coated papers are papers which, while having thereon a layer of mineral-coating comprising mineral pigment and adhesive in wet or plastic condition, have been pressed into adherent, non-slipping contact with a finishing surface, such as the surface of a polished metal drum or endless belt, and later have been removed from said finishing surface. Well-known examples of drum-finished mineral-coated papers are the "cast-surfaced" coated papers of commerce, the prototype of which was described in the Bradner U. S. Patent No. 1,719,166.

According to said patent a layer of aqueous mineral-coating composition comprising finely divided pigmentary matter such as clay and an adhesive such as solvated casein is applied to one side of a paper web and the wet coated side of the sheet is then pressed against a heated finishing surface, e. g. a chromium plated drum, where the coated surface remains in non-slipping, adherent contact until the coating has become dry whereupon the coated paper spontaneously releases from the finishing surface. Improvements on the process of the Bradner patent have been made as disclosed in the Warner Patent No. 2,316,202 and in the Leighton Patent No. 2,678,890. But these improvements retain the essential conditions of the Bradner patent that the wet coated surface is pressed into non-slipping adherent contact with a heated polished finishing surface against which it is dried and from which, when dry, it releases spontaneously.

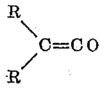
Unless precautions are taken, however, it frequently happens that the dried coated surface may stick in spots and not release spontaneously from the finishing surface, thus marring the surface of the coated paper when it is stripped from the finishing surface. Hence it is customary to follow the teaching of the Montgomery Patent No. 2,568,288 and maintain on the surface of the finishing drum an imperceptible film of oleaginous material to ensure that the coated surface will release satisfactorily from the finishing drum. The preferred practice according to the Montgomery patent is to include in the aqueous coating composition a small quantity of oleaginous release agent, say from 0.1 to 1.0% based on the dry weight of coating pigment. Sufficient oleaginous matter from the coating composition is adsorbed on the finishing surface to maintain a very thin imperceptible film thereon to facilitate release of the coated paper therefrom. According to the Montgomery patent the best oleaginous release agents were saponifiable materials like vegetable oil and fatty acids, and such agents were much superior to unsaponifiable oils such as mineral oils or to tributyl phosphate which was later disclaimed as a release agent in the Reissue Patent No. 23,637. As pointed out in the Montgomery patent almost any saponifiable matter which is included in the usual alkaline aqueous coating compositions will unavoidably be at least partially saponified even though unsaponified at the time of its addition to the coating composition.

Fats or oils saponified by alkali of course become soluble soaps which are exceptionally reliable release agents. There are, however, some undesirable effects attendent upon use of soluble soap in aqueous mineral-coating compositions. In the first place soap increases the tendency of the coating composition to foam, a tendency which even in the absence of added soap is liable to be troublesome. Anything which tends to increase trouble from foam obviously is to be avoided if possible. Soap remaining in the dried coating on the finished paper makes the coated surface unduly susceptible to moisture. Such susceptibility makes itself apparent in a tendency to be marked by damp fingers or other objects and is especially undesirable in paper which is to be printed by offset lithography, in which process the paper sheet comes into contact with a wet offset blanket.

The present invention makes use in the coating composition of a new release agent which is unsaponifiable but yet is comparable in effectiveness to the best saponifiable release agents hitherto used. Moreover, the new release agent performs a double function; besides facilitating release from the finishing surface it also greatly decreases the susceptibility of the finished coated paper to moisture. In other words, the presence of the new agent in the coating, instead of increasing moisture susceptibility like soap, actually imparts improved characteristics to the dried coated paper. The agent therefore serves a two-fold purpose so that two desirable effects are accomplished by the same double-acting agent.

The double-acting agents useful according to the inventions are selected from the class of dimers of aliphatic ketenes, in which the original ketenes have hydrocarbon groups containing from six to twenty carbon atoms inclusive. For convenience this class will hereinafter be referred to as the dimers of higher aliphatic ketenes.

The ketenes are compounds of the general formula



$$R_2C{=}CO$$

in which at least one R stands for an aliphatic hydrocarbon group and the other R stands for an aliphatic hydrocarbon group or hydrogen. The aliphatic hydrocarbon group or groups may be straight chain or branched chain or saturated or unsaturated. In other words the ketenes may be either keto or aldo alkyl or alkylene ketenes. The ketenes, the dimers of which are used (as sizing materials) in accordance with the present invention have hydrocarbon groups containing from 6 to 20 carbon atoms.

The ketenes and their dimers are well-known. They are described, for example, in Thorpe's "Dictionary of Applied Chemistry," vol. VII (published in 1946), pages 102–106; the "Journal of the American Chemical Society," vol. 69 (published in 1947), pages 2444–2448. Ketenes are also described in Gilman's "Organic Chemistry," vol. 1, second edition, published in 1943, pages 662–665.

The above mentioned ketenes, which have from six to twenty carbon atoms in their hydrocarbon groups are designated as the higher aliphatic ketenes for the purposes of this disclosure.

As stated above one R may be a hydrocarbon group and the other R may be hydrogen or both R's may be hydrocarbon groups and these hydrocarbon groups may be identical or different from each other.

For example, the ketene may be derived from oleic acid of which the formula is

$$CH_3(CH_2)_7CH{:}CH(CH_2)_7.COOH$$

The symbol R in the ketene formula would then represent $CH_3(CH_2)_7CH:CH(CH_2)_6$. This ketene and its dimer can be prepared as above described in the cited technical literature, and this dimer containing unsaturated hydrocarbon groups can be used in my invention.

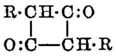
Other unsaturated fatty acids are well known. The ketenes derived from these unsaturated fatty acids can be dimerized and used in this invention.

Examples of ketenes having saturated hydrocarbon groups the dimers of which are usable in the present invention are hexyl, decyl, tetradecyl, hexadecyl and eicosanyl ketenes, to name only a few species of the group described above.

The use of emulsions which include said higher aliphatic ketene dimers is disclosed in Downey U. S. Patent No. 2,627,477 issued February 3, 1953, which refers to the formation of emulsions of said dimers in water by means of soap, synthetic detergents and other agents.

Many of the original ketenes of this class are disclosed in British Patent No. 522,204, accepted June 12, 1940.

The general formula of a ketene dimer of this class may be $RCH_2COCR:C:O$ as stated in the "Journal of the American Chemical Society," vol. 69, page 2444, although a more probable configuration is



In the above formulas, "R" represents the radical of a saturated straight-chain or branched chain hydrocarbon, or a radical which is unsaturated at one or more parts of its chain.

At ordinary room temperature of 20° C.–30° C., the dimers formed from higher aliphatic ketenes are oily liquids or solid and wax-like substances which can be melted at low temperature and which are stable when melted. These physical properties depend, at least in part, upon the degree of unsaturation of the fatty acids from which the original ketene monomers are derived. The ketene dimers most readily available at present are dimers of ketenes derived from stearic, palmitic, or oleic acids, or mixtures thereof.

In preparing aqueous coating compositions for use under the invention the ketene dimer in liquid form, heated if necessary for convenient use, may be stirred into an aqueous coating composition which includes pigment and an adhesive such as a protein or starch, with or without the addition of an emulsifying agent other than the adhesive already present. The preferred practice, however, is to make an aqueous emulsion or dispersion of the ketene dimer, and to mix said emulsion or dispersion into the aqueous coating composition.

One example of making an aqueous dispersion of a dimer is stated below:

In the following, the term "unit" refers to any unit of weight such as a pound or kilogram or the like.

Sixty units of the dimer of monohexadecyl ketene and twelve units of an emulsifying agent are mixed and heated to a temperature of 55° C. This operation, like all the operations disclosed herein, is performed under ordinary atmospheric pressure of approximately 760 millimeters of mercury. In this example, the emulsifying agent is polyoxyethylene sorbitan trioleate, which is known commercially as "Tween 85."

This emulsifying agent is an oily liquid at 25° C., with a specific gravity of 1.00 to 1.05 at 25° C. It is dispersible in distilled water. This "Tween 85" is fully described at page 587 of "Handbook of Material Trade Names" by Zimmerman & Lavine, published in 1953 by Industrial Research Service.

One hundred and twenty-eight units of water, which may be distilled water or tap water, are slowly added to the above mentioned mixture at 55° C.–60° C. The initial emulsion which is thus formed has a yellow color, and is a water-in-oil emulsion. When about half the water has been added, the emulsion becomes an oil-in-water emulsion, and the original yellow color changes to a white color. This emulsion can be used for the purposes of this invention.

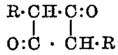
In this example, there are sixty units of the dimer in an emulsion whose total weight is 200 units. Hence, the weight of the dimer is 30% of the total weight of the emulsion. This is a convenient concentration of the dimer in the emulsion, but this ratio is not a sharply critical factor.

Another example of a satisfactory dispersion was made as follows:

Seven and a half units by weight of gum ghatti (an Indian gum derived from the tree *Anogeissus latifolia*) was swelled and dispersed in 205 units of water. This gum dispersion was then heated to 95° C. and there was then stirred into the dispersion 37.5 units of the melted dimer of the ketene derived from stearic acid. The resulting hot mixture was immediately passed through a homogenizer of the type used in dairies to homogenize milk. The effluent from the homogenizer was a stable, aqueous emulsion or dispersion of the ketene dimer.

Other examples of usable emulsions or dispersions of dimers are described in U. S. Patent No. 2,627,477.

In contradistinction to the non-polar, oily hydrocarbons which Montgomery did not find particularly effective as release agents, the ketene dimers are strongly polar compounds. Assuming that the configuration of the compounds may be represented by the formula,



it seems reasonable that when the compound is adsorbed on the finishing surface the ketone (C:O) groups at the middle of the molecule attach themselves to said finishing surface with the hydrophobic hydrocarbon groups at the ends of the molecule being exposed to the coated paper thereby to lessen the adherence therof to the finishing surface. It is also believed that similar orientation of the dimer molecule exists in the dried coating on the finished paper, whereby the molecule is affixed to the relatively hydrophilic components of the coating by means of its middle ketone groups, leaving its hydrophobic end groups free to repel water coming into contact with said coating. The action of the ketene dimer in the coated paper is very apparent in its effect on the contact angle which water makes with the surface. When drops of water are applied to the coated paper containing the dimer the drops tend to remain as individual droplets standing up on the coated surface, whereas similar drops applied to a coated paper, the coating of which contains no water-repellent agent, tend to flatten out and coalesce. The degree of water-repellence imparted to the coating by a small quantity of the dimer, say in the order of 1% of the dry weight of the coating, makes an important improvement in the suitability of the finished paper for use in offset lithography as well as in its behavior if accidently wetted by water.

An embodiment of the invention is shown by the following examples in which all units are units by weight.

Step 1

Eighteen units of casein were wetted with a solution of 3.6 units of dicyandiamide in 40 units of water. Dicyandiamide, or cyanoguanidine, is used to reduce the viscosity of the final aqueous coating composition; it is a common commercial chemical but its structural formula is not generally agreed upon. The wetted casein was mixed with 1.0 unit of 28% ammonia water at 50° C. until the protein was colloidally dispersed.

Step 2

Sixty-five units of fine-particle coating clay pigment and 35 units of fine-particle calcium carbonate pigment were mixed in a heavy-duty sigma-blade mixer with the dispersion of Step 1, and also with 40 units of water, to provide a thick mass.

Step 3

One-fourth of a unit of tributyl phosphate, an anti-foam agent, was mixed into the mixture of Step 2.

Step 4

There were added to the mixture of Step 3, 20 units of water and 10 units of an aqueous dispersion of the dimer of hexadecyl ketene containing 15% of the dimer which had been emulsified with gum ghatti as previously described.

Step 5

By means of a conventional transfer-roll coater the composition of Step 4 was applied in quantity amounting to about 25 grams, dry weight, per square meter, to one side of a well-formed web of paper of the quality commonly used as base for high grade coated papers. The so-coated web was then immediately run over a roll which pressed the coated side of said web into contact with the surface of a heated polished chromium plated drum. The surface of the coated paper at the line where it made contact with the drum was kept flooded with water according to the disclosure of aforementioned Leighton Patent No. 2,678,890. The coated paper remained in contact with the drum until the coating had become substantially dry, whereupon the paper released spontaneously from the drum.

The surface of the finished paper product was extremely glossy and entirely free from dull areas or spots caused by sticking of the coating to the drum. When the coated surface of the paper product was sprinkled with water droplets, the droplets retained their individuality without coalescing on the coated surface. The paper also was found to give excellent results when printed by offset lithography.

The coating composition of the preceding example can be varied considerably, as is well understood in the art. Pigments other than clay and calcium carbonate may be used, such as blanc fixe, satin white, titanium pigments and the like. Other adhesives may be used; the casein can be replaced by soy protein if desired or in part by starch, animal glue, or copolymer latex all as well known. The ratio of adhesive can be varied widely, from about 15 to 50 units for each 100 units of dry pigmentary matter.

The quantity of the ketene dimer release agent of the invention to be used is not as critical as in the case of the release agents disclosed in the Montgomery Patent No. 2,568,288 aforesaid. Useful quantities of higher aliphatic ketene dimer range from about 0.5 to about 3.0 units per 100 units of pigment in the coating composition. The exact quantity to be used depends upon the degree of water-repellence desired in the finished coating; less than 0.5 unit gives no appreciable water-repellence, whereas over 3.0 units makes the coating more water-repellent than is usually desirable in a printing paper.

Quantities anywhere in the range stated give good release from the finishing surface without causing any preceptible dulling of the coated surface.

I claim:

1. Process of making drum-finished mineral-coated paper which comprises moving a paper web bearing a coating in a wet and plastic state into non-slipping adhesive contact with a moving, heated, polished, finishing surface, drying the coating in contact with the finishing surface and separating the web and dried coating from the finishing surface, said coating consisting essentially of mineral pigment, hydrophilic adhesive of the group consisting of protein and starch and a dimer of a higher aliphatic ketene having a carbon chain of from 6 to 20 carbon atoms in the ratio of from 0.5 to 3 parts by weight of said dimer to each 100 parts by weight of pigment in the coating.

2. Cast-surfaced mineral coated paper consisting essentially of a paper web and a mineral coating thereon having a cast surface, said coating consisting essentially of mineral pigment, hydrophilic adhesive of the group consisting of protein and starch and a dimer of a higher aliphatic ketene having a carbon chain of from 6 to 20 carbon atoms in the ratio of from 0.5 to 3.0 parts by weight of said dimer to each 100 parts by weight of pigment in the coating.

3. Process as defined in claim 1 in which the proteinaceous adhesive is casein.

4. Process as defined in claim 1 in which the proteinaceous adhesive is soy protein.

5. Process as defined in claim 1 in which the proteinaceous adhesive is a mixture of casein and copolymer latex.

6. Process as defined in claim 1 in which the proteinaceous adhesive is a mixture of casein and starch.

7. Process as defined in claim 1 in which the proteinaceous adhesive is a mixture of casein and animal glue.

8. Cast-surfaced mineral coated paper as defined in claim 2 in which the proteinaceous adhesive is casein.

9. Cast-surfaced mineral coated paper as defined in claim 2 in which the proteinaceous adhesive is soy protein.

10. Cast-surfaced mineral coated paper as defined in claim 2 in which the proteinaceous adhesive is a mixture of casein and copolymer latex.

11. Cast-surfaced mineral coated paper as defined in claim 2 in which the proteinaceous adhesive is a mixture of casein and starch.

12. Cast-surfaced mineral coated paper as defined in claim 2 in which the proteinaceous adhesive is a mixture of casein and animal glue.

References Cited in the file of this patent

UNITED STATES PATENTS

Re. 23,637	Montgomery	Mar. 24, 1953
2,360,825	Blickensderfer	Oct. 24, 1944