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## PROCESS FOR TREATING FIBROUS PRODUCTS AND PRODUCT THEREOF

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The present invention relates to methods of imparting both grease resisting and water repellent properties to fibrous products. It also provides grease resistant and water repellent fibrous products such as textiles and papers.

At present processes related hereto generally deal with the treatment of textile fabrics for the development of water resistant or repellent properties and include the treatment of textile materials with condensation products of stearamide and formaldehyde and quaternary nitrogen compounds obtained by condensing stearamide, formaldehyde and pyridine. The above compounds are quite unstable, and although some are water soluble and some soluble in organic solvents they are somewhat difficult to apply to textiles and particularly to paper or paper fibers. Where paper and paper fibers are to be treated, simplicity of operation generally dictates the utilization of insoluble substances.

I have now found that if I employ an N,N' diacyl diamino methane where the acyl group is derived from acids ranging from C<sub>12</sub> to C<sub>28</sub>, I am able to obtain very superior results in the treatment of fibrous products, particularly where such treatment is carried out during the normal operations inherent in paper making. Because of the ready availability of technical stearic acid I prefer to prepare and to utilize technical N,N' distearoyl diamino methane, which is a colorless, white, crystalline, stable and substantially insoluble compound of pronounced hydrophobic character. However, other fatty acids such as oleic, lauric, montanic acid and related acids may be used in the preparation of the treating agents, as well as those derived from the commercial stearic acid, which commercial acid may contain appreciable amounts of palmitic acid. These diamide compounds may be conveniently made as shown by the following description:

N,N' diacyl diamino methanes may be prepared by any of several alternative processes involving the use of only the reactants or by effecting the condensation in either an organic solvent or an aqueous medium. As an example of a procedure for the preparation of N,N' dipalmitoyl diamino methane the following method may be used: In an open container fitted with a mechanical stirrer and a heating device 2000 cc. of water are charged and heated to 90° C. With the stirrer in motion 1000 grams of palmitamide are charged. Stirring is continued at 90° C. until a smooth dispersion is formed and then 90 cc. of concentrated hydrochloric acid and 325 cc. of 37% formalin are added at 90° C. Stirring is continued at 90° C. until the formation of a granular precipitate occurs. The charge is cooled and the product is filtered out, washed to neutrality and air dried. The yield of white prod-

uct melting at 139° C.-140° C. is practically quantitative.

Since the diamides of higher molecular weight, as prepared above, have pronounced hydrophobic properties, it is preferred for the application of these materials to fibrous products such as textiles, paper and paper pulp to utilize dispersing agents or wetting agents which may have the additional property of remaining in solution in the water without being adsorbed by the fibers at least to any considerable extent during application. According to my present understanding of the process for the development of permanent water repellent and grease proofing effects, the dispersion need only contain a minimum quantity of dispersing agent.

Suitable dispersing agents for the application of the diamides of higher molecular weight are the following: copolymers of styrene and maleic anhydride which have been converted to their water soluble salts, i. e., sodium or ammonium salts; organic amine salts of alkyl aryl phosphinic acids; sodium glyceryl sulforicinate, butyl hydroxy diphenyl sodium sulfonate, butyl diphenyl sodium sulfonate, dibutyl hydroxy diphenyl disodium disulfonates, and ammonium and organic amine salts of fatty acids such as ammonium, triethanol amine and morpholine salts of oleic acid.

The invention is illustrated by the following examples:

## EXAMPLE 1

A small amount of N,N' distearoyl diamino methane which is in a state of fine subdivision, is dusted upon a piece of normally absorbent paper and the excess of the diamide brushed off. It will generally be found that sufficient of the dry diamide is retained by adherence to the paper fibers so that after baking at about 150° C. for one minute surprising water repellent effects are obtained.

The above example illustrates the simplest application of my invention. For more lasting effects I prefer by one method to incorporate the diamides into the fluent pulp from which the paper sheet is to be formed. Accordingly the diamide prepared as described above, is added to the paper pulp in the beating engine or in the Jordan machine and thoroughly mixed with the pulp, or the diamide may be incorporated by applying as a water dispersion at the machine head box. The pulp is then sheeted on a screen, as in the Fourdrinier machine, dried and calendered at elevated temperatures and the resulting paper will be found to have excellent and permanent grease resisting and water repellent properties. Other methods of application of the diamide may be carried out by spraying a water dispersion of the diamide onto the paper web while it is being formed but before drying. Or it

may be applied as a tub-size to the dry finished paper by immersion in a bath containing the dispersion, followed by subsequent drying and calendering at elevated temperatures.

In testing the efficiency of a paper size, a common test which is applied is as follows: A paper dish is made by folding a small square of paper into a boat-like form which is then floated upon an ordinary liquid writing ink. The time necessary for the visible penetration of the ink through the paper boat is noted. Treated papers which have, when tested by this method, the longest interval between floating and the appearance of ink on the inside of the boat are considered the most efficient. For ordinary purposes a paper is considered satisfactory if the time of penetration is at least two minutes.

In testing the efficiency of a grease or oil resistant paper, it is customary to apply to such paper a solution of a dye in grease or in an oil such as paraffin or lubricating oil or in turpentine. The latter substance is generally employed because of the greater penetrating power of the turpentine. In order for the treated paper to be acceptable for general commercial usages, it is required that the paper exhibit no penetration to a solution of a dye in turpentine after an application of at least 1500 seconds.

For the production of papers having different degrees of grease or oil resistance, the content of the N,N' diacyl diamino methane in the paper may be varied. Satisfactory grease proofness may be obtained by the incorporation of from 1% to 3% through 5% to as much as 8% to 10% of the diamides.

In the application of my diamide to paper or paper pulp for the manufacture of grease resistant and water repellent papers, a heating or baking step is necessary wherein the temperature of the diamide and the paper is carried slightly above the melting point of the diamide. When the paper has been treated in the wet way, as by means of a paper coating machine, it is possible to combine the drying and the baking step in one operation. The drying operation may be carried out finally at temperatures slightly above the melting point of the diamide. Hence, when the N,N' distearoyl diamino methane, melting when pure at 146° C., is employed I prefer to dry the treated paper at temperatures in the neighborhood of 150° C. or even higher. Thus when utilizing temperatures of 150° C. for five minutes for the drying of the diamide treated paper, I have been able to obtain ink penetration values of five minutes and by a longer drying time at 150° C. I have obtained ink penetration values of approximately 20 minutes. Untreated paper of the same type shows an instantaneous penetration. When employing compounds produced from commercial mixtures of fatty acids, which generally melt at lower temperatures than the pure compounds, correspondingly lower baking temperatures may be employed.

#### EXAMPLE 2

A paper pulp consisting of 17.5 grams of rag pulp per gallon of water to which is added 0.7 gram of N,N' distearoyl diamino methane and 0.25 gram of the ammonium salt of the styrene maleic anhydride copolymer is sheeted upon a screen and the paper dried for five minutes at 150° C. The paper was found to possess an ink penetration value of five minutes. Upon drying the paper at 150° C. for 30 minutes, the ink penetration value had increased to 11 minutes.

Rag pulp paper is treated in the Example 2 above, as it is an example of a paper used largely for fine writing papers, and where the ordinary sizing of the same with the usual rosin sizes is particularly difficult. In many cases the degree of sizing need not be as great as indicated in this example. It may therefore be decreased by decreasing the concentration of the diamide incorporated with the pulp.

The process may be applied to various types of wood pulp fibers such as ground wood, sulfite, soda, kraft or sulfate pulps or even asbestos. In application it is generally sufficient to make an aqueous dispersion of the diamide in a colloid mill using the dispersing agents mentioned, or by the use of other known wetting out agents. The dispersion may be made in concentrated form, up to 40% or 50% solids, or in dilute form, say, from 1% to 4% solids and the dispersion then added to the pulp in the beater.

The fibers of the pulp and the paper prepared therefrom will in general be coated with the adherent particles of the diamide. The tenacity of adherence will depend, of course, upon the method of application employed, and can accordingly be varied somewhat. Where application of the diamide is made in the dry way, the adherence is generally at a minimum, so that abrasion or handling of the paper will generally somewhat decrease the water repellent and grease proof properties. This condition can be overcome by heating the treated paper to a temperature above the melting point of the diamide, or the mixture of diamides by which treatment the diamide is caused to flow in the molten state over the fibers, thus materially increasing the adherence of the diamide and consequently the permanency of the effects.

Other methods of increasing the permanency of the effects may, however, be employed. Such other methods may include the incorporation of various gums, resins or adhesives in or with the diamide or in the treating solution. Or such substances may be applied by an after treatment. The quantity of the diamide suspended in the pulp solution may be varied from a low value of 0.8% to 1% to a preferred 4% or 5% to a high value of 18% to 20%, depending upon the degree of water repellency or grease proofness desired. In general, the higher values are preferred for washable papers, as for example, washable wall papers.

#### EXAMPLE 3

A dispersion of 4 grams of N,N'-distearoyl-diaminomethane and 2 grams of water soluble salt such as the ammonium salt of the styrene maleic anhydride copolymer in 400 grams of water is prepared in the mechanical dispersing apparatus, after which the cloth is treated in a padding machine with the solution at a temperature of about 45° C. The cloth is wrung out and then heated to dry to a temperature of, say, 150° C., that is above the melting point of the diamide. It will be found to have a permanent, wash resistant, water repellent property and a good feel. Instead of employing a temperature above the melting point, I may employ a lower temperature, say, 120° C. to 130° C. for an increased length of time. During the heating step ammonia is evolved from the ammonium salt and the latter is probably changed to the insoluble free acid.

In order to measure the degree of effectiveness of my treatment as applied to textile products I utilize two tests which are generally accepted by

those skilled in the art. These tests are known as the spray test and as the hydrostatic head test. The spray test measures the amount of water absorbed by a standard sample of a treated cloth after the sample has been exposed to a spray of water for a specified length of time. The hydrostatic head test measures the hydrostatic head in centimeters of water which can be supported upon the treated fabric.

The spray test which I employ is described in the American Dyestuffs Reporter, vol. 28, page 285 for 1939.

The hydrostatic head test is described in the 1940 Yearbook of the American Association of Textile Chemists and Colorists at pages 223-4.

When the product as originally prepared in Example 1, is tested by these tests I obtain a moisture absorption by the spray test of 14.4% and a hydrostatic head test of 16.0 centimeters.

After subjecting my treated fabric to 20 consecutive washings with soap and water, I again tested the fabric and found that the moisture absorption, as measured by the spray test had increased to only 26.5% while the hydrostatic head test had decreased to only 10.5 centimeters.

#### EXAMPLE 4

A cotton fabric known as Indian head, is treated at a temperature of 65° C. with the same material, and afterwards with a 1% solution of aluminum sulfate. The treated fabric is tested with the results shown below. The aluminum sulfate produces an insoluble salt with the small amount of dispersing agent remaining on the cloth.

#### EXAMPLE 5

The same type of cotton fabric is treated as in Example 1 above, and afterwards with a 1% solution of CaCl<sub>2</sub>. In like manner the soluble calcium salt renders insoluble the residual maleic anhydride-styrene copolymer.

The results obtained upon testing the samples treated by my process are given in tabular form below:

*Waterproofing treatment of cotton fabric with 1% aqueous dispersions of distearoyl N,N'-diaminomethane*

| No.    | Dispersing agent                                                                                                                         | Temp. of application                                      | Evaluation     |                 |                       |                 |
|--------|------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------|----------------|-----------------|-----------------------|-----------------|
|        |                                                                                                                                          |                                                           | Spray test     |                 | Hydrostatic head test |                 |
|        |                                                                                                                                          |                                                           | Before washing | After 20 washes | Before washing        | After 20 washes |
| 1..... | NH <sub>4</sub> salt maleic anhydride styrene copolymer, 0.5%.....                                                                       | 45°.....                                                  | 14.4           | 26.5            | 16.0                  | 10.5            |
| 2..... | NH <sub>4</sub> salt maleic anhydride styrene copolymer, 0.1%.....                                                                       | 65°+Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ..... | 10.8           | 27.3            | 17.4                  | 15.5            |
| 3..... | do.....                                                                                                                                  | 45°+CaCl <sub>2</sub> .....                               | 11.4           | 30.3            | 17.4                  | 12.6            |
| 4..... | do.....                                                                                                                                  | 45°+Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ..... | 8.7            | 23.9            | 18.8                  | 15.0            |
| 5..... | C <sub>18</sub> H <sub>35</sub> O <sub>2</sub> PO <sub>2</sub> H <sub>2</sub> -NH <sub>2</sub> C <sub>4</sub> H <sub>9</sub> , 0.2%..... | 65°.....                                                  | 16.1           | 19.9            | 14.4                  | 14.8            |
| 6..... | C <sub>18</sub> H <sub>35</sub> O <sub>2</sub> PO <sub>2</sub> H <sub>2</sub> -NH <sub>2</sub> C <sub>4</sub> H <sub>9</sub> , 0.2%..... | 65°.....                                                  | 14.0           | 24.7            | 14.6                  | 10.3            |
| 7..... | Glyceryl sulfo ricinoleate, 0.25%.....                                                                                                   | 65°.....                                                  | 15.7           | 22.1            | 16.9                  | 14.4            |
| 8..... | Glyceryl sulfo ricinoleate, 0.125%.....                                                                                                  | 65°.....                                                  | 17.0           | 23.8            | 16.4                  | 12.8            |
| 9..... | Glyceryl sulfo ricinoleate, 0.025%.....                                                                                                  | 65°.....                                                  | 16.1           | 25.1            | 18.0                  | 15.0            |

The N,N'-diacyl diaminomethane may likewise be applied to the textile products woven or knitted from the synthetic linear condensation polyamide yarns, such as the polyhexamethylene adipamide for the purpose of increasing the water repellent properties thereof. Or it may be dispersed in the polymer or in solutions of the polymer which are later to be spun into filaments.

This may also be accomplished with other syn-

thetic textile products such as cellulose acetate, nitrate, viscose and in each case an improved water resistance may thereby be obtained. That is the diamide may either be applied by means of an after treatment or may be dispersed, as such, or with the aid of dispersing agents into the cellulosic ester where practical.

Because of the pronounced hydrophobic properties of the N,N'-diacyl diaminomethane already mentioned, advantage is taken, to as great an extent as practicable, of mechanical dispersing aids such as mixing devices, colloid mills, and the like. Such dispersion is preferably effected in the presence of the dispersing agents mentioned. The aqueous dispersion thereby obtained will contain the diamide compound and the dispersing agent, in the form of stable compositions.

Because of the pronounced heat stability of the diacyl diaminomethane herein disclosed, dispersions may be made by heating the diamide to temperatures above its melting point and then dispersing the molten diamide in water, in the presence of dispersing agents by the use of a high-speed agitator, homogenizer, etc.

While relatively dilute solutions of the dispersion, say, from 0.2% to 1%, or even 4% or 5% may be employed for the application of the cloth, even more concentrated dispersions say up to 40% or 50% may be advantageously prepared, which concentrated dispersions may be diluted to a satisfactory usable dilution prior to application to cloth. They may, of course, contain a quantity of dispersion agent, or not, as desired.

In general, suitable treating solutions may contain an amount of dispersing agent ranging from 1% to 10% or more by weight of the N,N'-diacyl diamino methane. Such treating solutions may conveniently be marketed directly as dispersions either in concentrated form or in dilute form ready for application to textiles. Or the dry powdered diamino methane may be marketed as such, or it may have mixed therewith a dispersion agent also in dry form, or the dry powdered diamino methane may, prior to drying be treated

with solutions of dispersion agent and then dried to obtain a dry powder of the N,N'-diacyl diamino methane upon the particles of which is coated the dispersion agent.

For practical purposes I prefer to prepare the diamides by utilizing a double pressed stearic acid or a product such as is known commercially as "Neo-Fats"—which are distilled fatty acid mixtures. The composition of representative sam-

ples of such fatty acids is approximately as follows:

|                                 | Neo-fats | Double pressed stearic acid |
|---------------------------------|----------|-----------------------------|
| Stearic acid..... per cent..... | 75.0     | 29                          |
| Palmitic acid..... do.....      | 22.0     | 65                          |
| Oleic acid..... do.....         | 3.0      | 6                           |
| Melting point..... °C.....      | 61.5     | 55-57                       |

These fatty acid mixtures may be converted to the amides by treatment with ammonia at elevated temperatures, and a mixture of amides in substantially the same proportions as given above for the acids, is obtained. Such a mixture of amides may contain some quantity of unreacted or free fatty acids, the amount being usually from 3% up to 16%. The free fatty acids may be removed from the amides or they may be permitted to remain therein. In the latter case, after condensation of the amides with formaldehyde, the fatty acids remain mixed with the condensation products. Condensation products containing the free fatty acid may be easily emulsified by the simple addition of a base such as organic bases, e. g., triethanolamine or inorganic bases, e. g., sodium hydrate.

By using a mixture of N,N' diacyl diamino methanes prepared from a mixture of fatty acid amides, such as above mentioned, an improved impregnation is readily obtained because of the lower melting point of the mixture.

Because of the oil and water resistant nature of the paper herein provided, it may be employed for the production of paper food or oil containers, for example, as for the packaging and shipment of food or oil.

Feeding and skin tests have shown that my products are non-toxic, when employed in the amounts necessary to obtain grease and water resistance.

By the term "paper" as used herein, I mean to include not only ordinary paper, but also cardboard or other thicker papers made from one or more plies of paper stock.

What I claim is:

1. A combined grease proof and water repellent paper containing a previously prepared N,N' diacyl diamino methane, where the acyl groups are those of from fatty acids ranging from C<sub>12</sub> to C<sub>28</sub>.

2. A combined grease proof and water repellent paper containing a previously prepared N,N' diacyl diamino methane, where the acyl groups are those of from a mixture of fatty acids including stearic and palmitic acids.

3. A combined grease proof and water repellent paper containing N,N' distearoyl diamino methane.

4. A combined grease proof and water repellent paper containing N,N' dipalmitoyl diamino methane.

5. The process of producing a combined grease resistant and water repellent paper comprising depositing upon said paper a minor amount of a previously prepared N,N' diacyl diamino methane, in which the acyl groups are derived from a C<sub>12</sub> to C<sub>28</sub> fatty acid, after which the paper is heated to a temperature above the melting point of the said N,N' diacyl diamino methane.

6. The process defined in claim 5 in which the compound deposited upon the paper is N,N' distearoyl diamino methane.

7. The process of producing a combined grease resistant and water repellent paper comprising treating a web of paper with an aqueous dispersion of a previously prepared N,N' diacyl diamino methane, in which the acyl groups are derived from a C<sub>12</sub> to C<sub>28</sub> fatty acid, after which the paper is dried and heated to a temperature above the melting point of the N,N' diacyl diamino methane.

8. The process defined in claim 7 in which the acyl groups are derived from a mixture of fatty acids including stearic and palmitic acids.

9. A fibrous product containing a previously prepared N,N' diacyl diamino methane, where the acyl groups are those of fatty acids ranging from C<sub>12</sub> to C<sub>28</sub>.

10. A fibrous product containing a previously prepared N,N'-distearoyldiaminomethane.

11. A textile treating product comprising an aqueous dispersion of an N,N' diacyl diamino methane, in which the acyl group is derived from acids having from 12 to 28 carbon atoms.

12. A textile treating product comprising an aqueous suspension of an N,N' diacyl diamino methane, in which the acyl group is derived from acids having from 12 to 28 carbon atoms, and a dispersing agent.

13. A textile treating product comprising an aqueous suspension of N,N'-distearoyldiaminomethane and a dispersing agent.

14. The process of imparting water repellent properties to fibrous products which comprises treating said products with an aqueous suspension of an N,N' diacyl diamino methane, the diacyl groups in said diamide being derived from a fatty acid having from 12 to 28 carbon atoms.

15. The process of imparting water repellent properties to textile products comprising forming an aqueous dispersion of N,N'-distearoyldiaminomethane and treating textile products therewith.

16. The process of imparting water repellent properties to textile products comprising forming an aqueous dispersion of an N,N' diacyl diamino methane, in which the acyl group is derived from acids having 12 to 28 carbon atoms, said dispersion also containing a small amount of a dispersing agent having wetting out properties and treating textile products therewith.

17. The process of imparting water repellent properties to textile products comprising treating said product with an aqueous dispersion of an N,N' diacyl diamino methane in which the acyl group is derived from acids having 12 to 28 carbon atoms and then drying and heating the treated product above the melting point of said diacyl diamino methane.

18. The process of imparting water repellent properties to a textile product which comprises treating said product with an aqueous dispersion of N,N'-distearoyldiaminomethane and then drying and heating the treated product above the melting point of said distearoyldiaminomethane.

19. The process of imparting water repellent properties to a textile product which comprises treating said product with an aqueous dispersion of an N,N' diacyl diamino methane in which the acyl group is derived from acids of 12 to 28 carbon atoms, said aqueous dispersion containing a dispersing agent having wetting out properties, and drying and heating the treated product at a temperature above the melting point of said diacyl diamino methane compound.

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