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GREASEPROOF AND WATER REPELLENT
PAPER

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The present invention relates to methods of imparting both grease resisting and water repellent properties to paper. It also provides grease resistant and water repellent papers.

At present processes related thereto 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 or with the quaternary nitrogen compounds obtained by condensing stearamide, formaldehyde and pyridine. The above compounds are quite unstable, and although some are water soluble and some are 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-acylated ortho- or para-aminobiphenyl where the acyl group is derived from acids ranging from C₁₂ to C₂₈, I am able to obtain very superior results in the treatment of paper, 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-stearoyl ortho-, meta- or para-aminobiphenyl, which compounds are colorless, or white, substantially insoluble materials 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 N-acylated aminobiphenyls may be prepared by any of several alternative processes. The N-acylated-p-aminobiphenyls, for example, may be prepared by the reaction of p-aminobiphenyl with an acyl halide of from 12 to 28 carbon atoms in known manner. The N-acylated-o-aminobiphenyls are advantageously prepared according to the method described in a copending U. S. application of C. A. Hochwalt, Serial No. 435,836, filed March 23, 1942, i. e., by the reaction of o-aminobiphenyl with a fatty acid glyceride having from 12 to 28 carbon atoms in the acid group, or with the pure acids, or with a technical mixture of such acids, or acyl halides thereof.

Since these higher N-acylated ortho- or para-aminobiphenyls, have pronounced hydrophobic properties, it is preferred for the application of

these materials to 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.

10 Suitable dispersing agents for the application of the N-acylated aminobiphenyls are the following: copolymers of styrene and maleic anhydride which have been converted to their water soluble salts, i. e., sodium or ammonium salts; 15 organic amine salts of alkyl aryl phosphinic acids; sodium glyceryl sulforicinate; butyl hydroxy biphenyl sodium sulfonate; dibutyl hydroxy biphenyl disodium disulfonates; and ammonium and organic amine salts of fatty acids such as ammonium, triethanolamine and morpholine salts of oleic acid.

The invention is illustrated by the following examples:

Example 1

25 A small amount of N-stearoyl-o-aminobiphenyl which is in a state of fine subdivision is dusted upon a piece of normally absorbent paper and the excess of the amide is brushed off. It 30 will be found that sufficient of the dry amide is retained by adherence to the paper fibers so that after baking at about 100° C. for one minute surprising water repellent effects are obtained.

The above example illustrates the simplest 35 application of my invention. For more lasting effects I prefer, by one method, to incorporate the amide into the fluent pulp from which the paper sheet is to be formed. Accordingly, the amide is added to the paper pulp in the beating engine or 40 in the Jordan machine and thoroughly mixed with the pulp, or the amide 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 45 paper will be found to have excellent and permanent grease resisting and water repellent properties. Other methods of application of the amide may be carried out by spraying a water 50 dispersion of the amide 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, by means of a paper coating machine, followed by 55 subsequent drying and calendering at elevated

temperatures. Also, the amide may be melted and applied to the paper or to the paper forming fiber by immersion of the same into the molten amide.

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 a 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-acylaminobiphenyl 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 amide.

In the application of my amides 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 amide and the paper is carried slightly above the melting point of the amide but below the temperature at which the paper is scorched or tendered. Where 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 should then be carried out at temperatures slightly above the melting point of the amide. Hence when the N-stearoyl-o-aminobiphenyl, melting when pure at 80° C., is employed, I prefer to dry the treated paper at temperatures in the neighborhood of 90° C. or even higher. Thus when utilizing a temperature of 100° C. for 10 minutes for the drying of the amide-treated paper, I have been able to obtain turpentine-dye penetration values of greater than 25 minutes. When employing compounds produced from the 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 10% dispersion of N-stearoyl-o-aminobiphenyl (prepared by reaction of o-aminobiphenyl with technical stearic acid) was prepared from 10 g. of the amide, 1 g. of stearic acid, 0.5 g. of triethanolamine and 88 g. of water. The dispersion was painted on a piece of onion skin paper which was then dried under an infra-red light and then baked for 10 minutes at a temperature of 100° C. Turpentine does not penetrate the treated sheet in 25 minutes. Untreated paper of the same type shows an instantaneous penetration.

Example 3

10 g. of crude N-stearoyl-p-aminobiphenyl, 1 g. of stearic acid, 2 cc. of concentrated ammonium hydroxide and enough water to make up 100 g. of mixture were dispersed by use of a Waring Blendor. A piece of onion skin paper was coated with the dispersion and baked for 10 minutes at a temperature of 150° C. The treated paper resists penetration of turpentine for 25 minutes.

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 amide in a colloid mill using the dispersing agents mentioned, or by the use of other known wetting 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 amide. The tenacity of adherence will depend, of course, upon the method of application employed, and can accordingly be varied somewhat. Where application of the amide is made in the dry way, the adherence is generally at a minimum, so that abrasion or handling of the paper will generally 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 amide, or the mixture of amides, by which treatment the amide is caused to flow in the molten state over the fibers, thus materially increasing the adherence of the amide 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 amide or in the treating solution. Or such substances may be applied by an after treatment. The quantity of the amide suspended in the pulp solution may be varied from a low value 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.

For practical purposes I prefer to prepare the amides 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 samples of such fatty acids is approximately as follows:

	Neo-fats	Double pressed stearic acid
Stearic acid.....percent.....	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 o- or p-aminobiphenyl 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 free fatty acids may be removed from the amides or they

may be permitted to remain therein. 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-acylated ortho- or para-aminobiphenyls prepared from a mixture of fatty acids, 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 necessary amounts 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 whether made from one or more plies of paper stock.

What I claim is:

- 5 1. A combined grease proof and water repellent paper containing an N-acylated aminobiphenyl where the acyl group is that of fatty acids ranging from C₁₂ to C₂₈.
- 10 2. A combined grease proof and water repellent paper containing an N-acylated aminobiphenyl, where the acyl groups are those of a mixture of fatty acids including stearic and palmitic acids.
- 15 3. A combined grease proof and water repellent paper containing N-stearoyl aminobiphenyl.
4. A combined grease proof and water repellent paper containing N-stearoyl orthoaminobiphenyl.
5. A combined grease proof and water repellent paper containing N-stearoyl para-aminobiphenyl.

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