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2,840,138

WILTPROOFING PAPER AND METHOD OF CORRUGATING

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This invention relates to the treatment of paper and paperboard sheets or webs hereinafter referred to as paper, with a molten, plasticized, resinous composition. The invention is concerned not only with the treating process and with the treated product, but also with the hereinafter-described treating compositions.

A problem of considerable importance to the paper and paperboard industry is the tendency of the paper to wilt under conditions of high humidity. The paper tends to absorb moisture from the air, with the result that the paper fibers soften and lose their stiffness. Obviously, the ultimate effect is a weakened paperboard structure which will not retain its shape under normal handling in transit and storage.

Heretofore, various resinous compositions have been suggested for use in the molten state to impregnate paper. However, of the known resinous compositions, none have obtained commercial success because of one or more of several disadvantages. Substantially thorough impregnation of the paper must be obtained in order to effectively protect the fibers from the absorption of moisture and to effectively stiffen the sheet. The ability of the molten resinous composition to penetrate and impregnate the paper is related to the viscosity of the composition. Accordingly, the resinous composition in its molten state must have a viscosity such that it will penetrate and become impregnated or embodied in the paper. Increasing the temperature of a molten resin, of course, decreases its viscosity. However, for paper impregnation purposes, the temperature of the molten resin is seriously limited to a low maximum temperature. The temperature of the molten resin should not exceed that temperature at which the paper will char or otherwise become heat-damaged. The disadvantage of many of the known molten resin impregnating compositions is that the resin compositions have high-melt temperatures and also high-melt viscosities. Thus, in order to obtain substantial wilt-proofing of paper, the molten resin composition must have a low-melt temperature and a viscosity at low temperature which will permit rapid and substantially thor-

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ough impregnation or penetration of the paper by the molten resin composition.

The impregnating material should not form a glossy-type coating on the surface of the paper. In the production of corrugated paperboard, solid fibreboard and related products, it is essential that the surface of the impregnated paper be compatible with a combining adhesive subsequently used in the production of manufactured items. That is, the impregnated paper should have the fibers exposed so that the paper will accept the adhesive and bind itself to other paper liners.

A further disadvantage of some impregnating agents is that the presence of the impregnating agents prevents the repulping of the impregnated paper for re-use.

The composition of this invention, comprising fatty acid plasticized, pine-wood-type resin, has been found to give excellent wilt-resistant properties to paperboard and paper. The plasticized resin composition in a molten state is applied to the surface of the paper in the form of a coating, and then heat treated to cause the plasticized resin to impregnate and penetrate into the paper without the formation of a glossy-type coating. Accordingly, an object of this invention is to provide a wilt-resistant paper. A further object is to provide a plasticized resin treated paper, which is characterized by increased rigidity, even when in contact with an atmosphere of high humidity. An additional object of this invention is to obtain an impregnated paper which does not have a glossy-type coating and which is compatible with combining or laminating adhesives. A further advantageous feature is that the impregnated paper of this invention is capable of being repulped for re-use. As will become apparent from the following disclosure, an object realized is the application of the molten, plasticized resin to the paper at relatively low temperatures, which will not char or otherwise heat-damage the paper. It will be obvious to those versed in the paper-making and paper-converting arts that the original strength or rigidity of untreated paper will be a determining factor, together with other factors, governing rigidity and strength characteristics of the treated sheet of paper.

Other objects and advantages will become apparent from the following detailed disclosure and examples.

In the following table are set forth examples of various compositions of the plasticized resin of the present invention. The paper used in accordance with these examples is that paper which is used in the manufacture of corrugated fibreboard commonly known as semi-chemical corrugating material or medium. Paper made by other well-known processes such as kraft paper, straw paper, repulped waste papers, etc., may be used. The percentage values given in the table are based upon percentage by weight.

Table

Ex.	Formula composition		Plasticizer—Percent composition										Test data					
	Per-cent resin	Per-cent plas-ticizer	Ca-rylic	Cap-ric	Lau-ric	My-ristic	Pal-mitic	Ste-aric	Oleic	Lin-oleic	Lino-lenic	Satur-ated fatty acid mixture	Penetration		Flow point, ° F.	Concora medium test		
													Sec.	Per-cent		Imme-diate	R. H., 50%	R. H., 85%, 3 days
1	60	40					22	75	3				3.00 to 4.00	3.00	70	179	98.7	38.7
2	60	40					53	42	5					4.00	80-85	187	99.3	37.0
3	60	40					54	43	3					3.00	75	178	103.7	52.0
4	50	50					54	43	3					3.00	80	192	99.7	47.7
5	30	70					54	43	3					3.00	95	203	108.7	51.0
6	70	30					54	43	3					3.00	70	186	96.3	50.7
7	80	20					54	43	3					3.00	60	200	78.3	41.7
8	90	10					54	43	3					3.00	40-50	235	90.7	31.3
9	60	40					92	6	2					3.43	90	170	89.3	35.3
10	60	40					60	36	4					3.62	85-90	186	111.0	43.0
11	60	40					32	64	4				2.72	80-90	196	98.0	40.7	
12	60	40					23	75	2				2.64	60-70	190	101.3	41.3	
13	60	40					8	90	2				2.62	85	200	100.3	37.3	
14	60	40			3	2	30	15	50				2.25	70	172	58.0	27.5	
15	60	40			4	91	5						2.58	90	158	96.0	45.0	
16	60	40	8	7	49	17	9	2	6	2			3.75	50	136	54.8	27.8	
17	60	40							50	48			3.00	60-70	184	57.0	28.0	
18	60	40							38	6	1	55	2.69	50-60	169	63.6	33.4	
19	60	40						100					2.62	80-90	187	93.7	38.3	
20	60	40					55	45	(2)				2.93	80-85	188	96.3	39.7	
21	60	40					(2)	(2)	(2)				2.52	50	168	67.3	28.0	
22	Blank															54.3	43.4	26.0

* Rubber grade.
* Tallow fatty acids.

The resin used in the examples is an extracted pine-wood-type resin, hereinafter referred to as "substantially petroleum hydrocarbon insoluble pine wood resin." This resin is that which is isolated from pine wood in the following manner: The pine wood, which may or may not have been steamed to remove volatile constituents, such as turpentine and pine oil, is extracted with a coal tar hydrocarbon, such as benzene or toluene, and the extract is then freed of volatile constituents, leaving a resinous residue consisting of a mixture of wood rosin and the resin used in the present composition. The rosin is dissolved and removed from the residue by extraction with a petroleum hydrocarbon, such as gasoline. The resinous residue remaining after the petroleum hydrocarbon extraction is low in abietic acid. This resin, low in abietic acid, is the resin which comprises the resin employed according to the present invention. Other known methods of isolating this resin may be employed. The particular resin used in the examples is that which is sold under the trademark "Vinsol," and marketed by Hercules Powder Company, of Wilmington, Delaware.

The fatty acids and mixtures of fatty acids function as a plasticizer or introfier for the resin. The fatty acid plasticizing agents enable the resin to quickly penetrate the surface of the paper and cause substantially thorough impregnation of the resin throughout the paper at relatively low temperatures. The preferred fatty acids useful for the plasticization or introfaction of the substantially petroleum hydrocarbon insoluble pine wood resin for the purposes of this invention are the saturated and unsaturated fatty acids having from eight to eighteen carbon atoms. As shown in the table, the fatty acid content of the compositions may vary from 10 to 70 percent of the total, by weight, with the balance being the substantially petroleum hydrocarbon insoluble pine wood resin. For the reasons which will appear below, the preferred composition is that which has a fatty acid content of approximately 30 to 50 percent.

The plasticized substantially petroleum hydrocarbon insoluble pine wood resin is applied to the paper in a molten state. Plasticization of the resin may be accomplished by heating a mixture of the unmelted resin and the fatty acid plasticizing agent. The mixture is stirred sufficiently to obtain a uniform dispersion of the plasticizing agent in the resin. The molten plasticized resin is maintained at a temperature below that which will char

or burn the paper, preferably about 325° F. to 335° F., although temperatures as high as 400° F. to 415° F. have been used. After the plasticized resin is applied to the surface of the paper in the form of a coating, the coated paper is heat treated to cause the plasticized resin to become impregnated in the paper. Again, in the practice of this invention, the temperature of the heat-treating step need not be in excess of that temperature which will heat-damage the paper, but, of course, should be above the flow-point temperature of the plasticized resin. In the examples cited in the table, a method using a minimum of operational steps was used. In the method used, the paper is passed between two hot rolls. The lower roll is in contact with, or partially submerged in, a molten bath of the plasticized resin. The lower roll serves to pick up the molten plasticized resin and coat the side of the paper which is passed in contact with the lower roll. The upper roll may be used to cause partial impregnation of the plasticized resin as it is coated on the paper by pressing the paper upon the lower pick-up roll. The paper may then be continuously brought into contact with another heated roll. This subsequent contact with the heated roll constitutes the heat-treating step which causes the impregnation of the plasticized resin into the paper. The impregnated paper does not have a glossy coating over the surface. The surface of the paper advantageously retains its compatibility with combining or laminating adhesives.

This example describes an application method for coating and impregnating one side of the web under treatment. It will be understood that provision for application of the molten, plasticized, resinous impregnating composition to either one side or both sides of the web receiving impregnation shall be within the scope of this invention.

In the table, Examples 1 through 13 show a variety of mixtures of palmitic, stearic, and oleic acids as plasticizing agents combined in various proportions with the substantially petroleum hydrocarbon insoluble resin. Examples 14 through 16 are directed to plasticizing agents containing lower fatty acids, the lowest fatty acid having a minimum of eight carbon atoms. Examples 17 and 18 are directed to plasticizing agents containing the higher fatty acids, the highest fatty acid having a maximum of eighteen carbon atoms. The plasticizing agents of Examples 17 and 18 also contain an amount of miscellane-

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ous saturated fatty acids. The number of carbon atoms in these miscellaneous fatty acids also varies from eight to eighteen carbon atoms. The fatty acids of Example 17 are commonly known as tall oil fatty acids. The fatty acids of Example 18 are those derived from distilled palm oil and are commercially available under the trade name "Emery 640," marketed by Emery Industries, Inc. The plasticizing agent of Example 19 is rubber grade stearic acid and is available from a number of commercial sources, such as General Mills, Inc. Example 20 shows a plasticizing agent consisting of palmitic and stearic acids in about equal proportions. Example 21 is illustrative of a plasticizing agent consisting of a mixture of fatty acids present in tallow, commonly known as tallow fatty acids. Example 22 is an untreated sample of the corrugating material. Its wilt-resistant characteristics are given for purposes of comparison with the same paper treated in accordance with the present invention.

Reference to the test-data columns shows the rapidity at which the plasticized resin composition penetrates and impregnates the paper. The time of penetration is determined by pressing a 4-inch by 6-inch piece of paper as it comes from the pick-up roll against a stationary roll which is maintained at a temperature of 330° F. This temperature is well within the range of temperatures which will not char or otherwise heat-damage the paper. The degree or percent of penetration of the plasticized resin into the paper is determined by measuring the extent to which the impregnating material soaks or migrates into a sheet of paper. For example, a 10-point sheet (.010-inch thick) which is impregnated in accordance with the present invention to a depth of 8 points (.008 inch) has an 80 percent penetration of the plasticized resin.

In addition to functioning as a plasticizing agent for the substantially petroleum hydrocarbon insoluble pine wood resin, the fatty acids affect a lowering of the flow-point temperature of the resin. In comparison with the values of the table, the flow point temperature of the unplasticized resin is 240° F. A fatty acid content of 30 to 50 percent provides an adequate lowering of the melt temperature to give a satisfactory degree of impregnation for waterproofing the paper.

The temperature at which the plasticized resin will begin to flow is determined by a modified Columbia method. In this method a 1-inch test tube is supported in the center of a beaker filled with mineral oil. A thermometer bulb is two-thirds coated by dipping into the molten plasticized resin, and removing at a slow, even rate. When cool, the thermometer is then suspended in the center of the test tube. The mineral oil is then heated, and the temperature at which a drop of the plasticized resin falls from the thermometer bulb is recorded as the flow point.

The wilt-resistant and crush-strength properties of the plain and impregnated corrugating material paper were determined by the Concora Medium Test. Essentially, this test consists of cutting an accurate 6-inch by ½-inch specimen and then corrugating the specimen through a fluter. The corrugated sample is placed on a rack with flutes matching the configuration of the sample. A comb is placed over the sample to hold it in place and a strip of ¾-inch wide tape is adhered to it. Then the comb is removed and the resulting sample strip of so-called single face is placed between the platens of a flat crush tester. The force in pounds necessary to crush the sample is the test result. This testing procedure is more particularly described in the article entitled "A new test for corrugating medium," by F. D. Long and G. G. Maltenfort, published in *Fiber Containers and Paperboard Mills*, pp. 86 to 92 (December 1952). Specimens of each of the examples were subjected to flat crush testing immediately after Concora fluting and single face sample fabrication. Other specimens of each of the examples were tested after 1 day's exposure to 50 percent

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relative humidity to bring the specimens to a state of moisture equilibrium therewith. In addition, specimens of each of these examples were tested after three days' exposure to the extreme condition of 85 percent relative humidity. The values for these tests are set forth in the last three columns of the table. The Concora Medium Test results for untreated corrugating material paper are recorded as Example 22. Comparison of these values for Examples 1 through 21 with the values for the untreated corrugating material paper of Example 22 shows the improved wilt-resistant properties of the paper treated with the fatty acid plasticized resin of the present invention.

Examples given in this specification are illustrative of the plasticized resinous impregnating composition disclosed herein, but are not to be construed as limiting said impregnation composition.

It will be understood that impregnation or treatment of paper components subsequently to be combined or laminated into corrugated fibreboard and/or solid fibreboard and utilized as such shall be within the scope of this invention. Conventional use of the impregnated paper component in corrugated fibreboard shall be as the inner component of the fibreboard known as corrugated material, but the other components can receive like treatment also. The commercial material known as solid fibreboard differs from corrugated fibreboard in that all plies of the solid fibreboard are in intimate continuous contact one with the other. Any one or all of the component paperboard plies of fibreboard can be impregnated by methods disclosed herein prior to final combination as the said solid fibreboard.

In summary, it is seen that the fatty acid plasticizing agent enables the resin to easily and quickly penetrate into the paper. The process of impregnating the paper involves a minimum of procedural steps and, therefore, has the advantage of being adapted to use with existing commercial equipment. The fatty acid plasticized substantially petroleum hydrocarbon insoluble pine wood resin imparts increased wilt-resistant properties to the paper as evidenced by the increased strength and rigidity of the treated paper under conditions of exposure to normal and relatively high humidity.

What is claimed is:

1. The method of imparting wilt-resistant properties to paper comprising coating the paper with molten plasticized resin, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance at least one fatty acid as a plasticizer, and thereafter contacting the coated paper against a heated surface to impregnate the paper with said resin.
2. The method of imparting wilt-resistant properties to paper comprising coating the paper with molten plasticized resin, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance at least one fatty acid having from 8 to 18 carbon atoms as a plasticizer, and thereafter contacting the coated paper against a heated surface to impregnate the paper with said resin.
3. The method of imparting wilt-resistant properties to paper comprising coating the paper with molten plasticized resin, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance stearic acid as a plasticizer, and thereafter contacting the coated paper against a heated surface to impregnate the paper with said resin.
4. The method of imparting wilt-resistant properties to paper comprising coating the paper with molten plasticized resin, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance a mixture of lauric, myristic, and palmitic acids as a plasticizer, and

thereafter contacting the coated paper against a heated surface to impregnate the paper with resin.

5. The method of imparting wilt-resistant properties to paper comprising coating the paper with molten plasticized resin, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance tallow fatty acids as a plasticizer, and thereafter contacting the coated paper against a heated surface to impregnate the paper with said resin.

6. In a method of making corrugating material for corrugated fibreboard construction, the step of imparting wilt-resistant properties to said corrugating material comprising impregnating paper with molten plasticized resin, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance at least one fatty acid as a plasticizer, and corrugating the impregnated paper.

7. In a method of making corrugating material for corrugated fibreboard construction, the step of imparting wilt-resistant properties to said corrugating material comprising impregnating paper with molten plasticized resin, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance at least one fatty acid having from 8 to 18 carbon atoms as a plasticizer, and corrugating the impregnated paper.

8. A corrugating material comprising plasticized resin impregnated paper, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance at least one fatty acid as a plasticizer.

9. A corrugating material having improved wilt-resistant properties comprising plasticized resin-impregnated paper, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance at least one fatty acid having from 8 to 18 carbon atoms as a plasticizer.

10. A corrugating material having improved wilt-resistant properties comprising plasticized resin-impregnated paper, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance stearic acid as a plasticizer.

11. A corrugating material having improved wilt-resistant properties comprising plasticized resin-impregnated paper, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance a mixture of lauric acid, myristic acid, and palmitic acid as a plasticizer.

12. A corrugating material having improved wilt-resistant properties comprising plasticized resin-impregnated paper, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance tallow fatty acids as a plasticizer.

13. A paperboard sheet suitable for use as at least one of the facing components of corrugated fibreboard, said sheet comprising plasticized resin-impregnated paperboard, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance at least one fatty acid as a plasticizer.

14. A paperboard sheet suitable for use as at least one of the facing components of corrugated fibreboard, said sheet having increased wilt-resistant properties comprising plasticized resin-impregnated paperboard, said plasticized resin comprising from about 30 to 90 percent of sub-

stantially petroleum hydrocarbon insoluble pine wood resin and the balance at least one fatty acid having from 8 to 18 carbon atoms as a plasticizer.

15. Paper suitable for inclusion as at least one of the components of fibreboard, said paper comprising plasticized resin-impregnated paper, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance at least one fatty acid as a plasticizer.

16. Paper suitable for use as at least one of the components of fibreboard, said paper having increased wilt-resistant properties comprising plasticized resin-impregnated paper, said plasticized resin comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance at least one fatty acid having from 8 to 18 carbon atoms as a plasticizer.

17. A hot-melt resinous composition for wilt-proofing paper or paperboard comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance at least one fatty acid as a plasticizer, said composition characterized by a low-melt viscosity below that of said pine wood resin without said plasticizer and the ability to rapidly penetrate and impregnate the paper.

18. A hot-melt resinous composition for wilt-proofing paper or paperboard comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance at least one fatty acid having from 8 to 18 carbon atoms as a plasticizer, said composition characterized by a low-melt viscosity below that of the said pine wood resin without said plasticizer and the ability to rapidly penetrate and impregnate the paper.

19. A hot-melt resinous composition for wilt-proofing paper or paperboard comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance stearic acid as a plasticizer, said composition characterized by a low-melt viscosity below that of the said pine wood resin without said plasticizer and the ability to rapidly penetrate and impregnate the paper.

20. A hot-melt resinous composition for wilt-proofing paper or paperboard comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance a mixture of lauric, myristic, and palmitic acids as a plasticizer, said composition characterized by a low-melt viscosity below that of the said pine wood resin without said plasticizer and the ability to rapidly penetrate and impregnate the paper.

21. A hot-melt resinous composition for wilt-proofing paper or paperboard comprising from about 30 to 90 percent of substantially petroleum hydrocarbon insoluble pine wood resin and the balance tallow fatty acids as a plasticizer, said resin composition characterized by a low-melt viscosity below that of the said pine wood resin without said plasticizer and the ability to rapidly penetrate and impregnate paper.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,840,138

June 24, 1958

Herbert N. Johnston et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 75, for "after 1 day's exposure to 50 percent" read
-- after exposure to 50 percent --.

Signed and sealed this 9th day of September 1958.

(SEAL)

Attest:

CARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents