

[54] **METHOD OF MAKING A HYDROPHOBIC FIBROUS PRODUCT**

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[51] Int. Cl. **D21d 3/00**

[58] Field of Search **162/100, 183; 34/10, 34/13.8; 210/DIG. 21; 252/427**

[56] **References Cited**

UNITED STATES PATENTS

3,440,135	4/1969	Chung.....	162/183 X
3,497,418	2/1970	Thale et al.....	162/100
2,447,161	8/1948	Coghill.....	162/213

3,445,330	5/1969	Kulick et al.	162/164
3,591,524	7/1971	Eriksen	210/DIG. 21

OTHER PUBLICATIONS

Casey, James P. *Pulp and Paper Vol. II, Second Edition* Interscience Publishers Inc., New York, N.Y. 1960 pp. 1052-1054.

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[57] ABSTRACT

A method for making a hydrophobic fibrous material is disclosed wherein a wet pulp is treated with conventional chemical sizing materials and thereafter the pulp is flash dried. The sized, flash dried hydrophobic fibrous material may be used to sorb oil from the surface of water.

6 Claims, No Drawings

METHOD OF MAKING A HYDROPHOBIC FIBROUS PRODUCT

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method for making sized, dried fibrous material. More specifically, this invention is for a process for flash drying sized lignocellulosic material, for example, wood pulp.

2. The Prior Art

The problem of removing oil from the surface of water is well known, as in the case of large oil spills considerable damage to beaches and wildlife may occur. Suggested solutions to this problem include materials for adsorbing or absorbing oil, such as wheat straw, foams from polyurethane and polyethylene, talc, silicone treated pumice or perlite, and silicone treated cellulose fibers to name a few. Most of these materials have a bulk density of 0.5 pounds per cubic foot to 7 or so pounds per cubic foot. Their bulk densities to a large extent determine their effectiveness on sorbing oil, i.e., pounds of oil sorbed per pound of material, which runs from about 5 to about 15, although other factors, such as the relative hydrophilic or hydrophobic nature of the surfaces of the product and the pore volume of the structure are important factors.

The general object of this invention is to provide a method of making a hydrophobic lignocellulosic fibrous product. Another object of this invention is to provide a lignocellulosic material that is both lyophilic and hydrophobic for use in removing oil from water. Still another object of this invention is to provide a material which will sorb up to 20 times its own weight of oil on a water surface and remain floating.

Other objects, features and advantages of this invention will become apparent from the following detailed description.

SUMMARY OF THE INVENTION

It has been found that a hydrophobic fibrous product may be made by flash drying a slurry of sized pulp. It has also been found that such a sized and flash dried lignocellulosic material has the capacity to sorb oil from the surface of water and remain floating. It is preferable that the lignocellulosic material be a pulp, sized with at least 0.05 percent and preferably about 1.0 percent by weight of a conventional papermaking size, the desired amount of sizing depending upon the efficiency of the size used and the degree of hydrophobic properties desired. It is understood that increased amounts of size may be used, but such increases do not generally increase the effectiveness of the product and are economically wasteful. Such sized and flash-dried fibers are able to absorb about 20 times their own weight of oil. Dried pulp which is not sized does not sorb the oil from the water surface, but rather disperses in the water phase and sinks. There are numerous applications this product in recovery of oil from water. For example, oil might be recovered from oil spills from water transport vessels and from oil present in effluents of oil refiners.

DETAILED DESCRIPTION OF THE INVENTION

When sized with conventional papermaking sizes for example, acid anhydride sizes, rosin and alum sizes, or self-sized, for example, by use of alum to fix natural or

ganic sizing materials which may be present as impurities in the pulp, lignocellulosic materials fluffed and then flash dried, float on top of water and have the ability to sorb oil from the water surface. By "sorb" it is meant the oil is held by the lignocellulosic material through absorption or adsorption. Unsized lignocellulosic materials fluffed and dried in a similar manner, sink without sorbing any oil from the layer on the top of the water.

The preferred oil absorbing lignocellulosic material is produced from ground wood, sawdust or conventional chemical pulps which are bleached or unbleached, sawdust pulps and high yield semichemical or mechanical pulps. The nature of the pulp used does not appear to be an essential aspect of this invention and the fiber could be a by-product or waste product such as the fiber reclaimed from waste treatment clarifiers or similar fiber reclaiming devices. Further, complete separation of fibers in the raw material should not be necessary and pulps containing fiber bundles should be equally useful.

The sizing materials contemplated for use in this invention include synthetic sizes, mainly fatty acid anhydrides, dimer sizes, rosin and modified rosin sizes, other tall oil derived sizing materials, and asphaltic sizing materials, such as are often used in the process and art of papermaking. The application and technology of such sizing compounds is reviewed in TAPPI Monograph No. 33, Internal Sizing of Paper and Paperboard (1971).

The amount of size used depends upon the effectiveness of the particular sizing material. For example, for stearic acid anhydride size approximately 0.5 percent size is required in pulp to be able to sorb 10 milliliters of oil per 1 gram of dried fiber. When using an asphalt-based size up to 5.0 percent by weight is required for the same degree of effectiveness. The expressed amount of size in pulp is the applied amount assuming 100 percent retention of the size. One effective product is a self-sized fiber, i.e., sized by addition of alum to fix the naturally occurring resins or fatty acids which occur in some pulps, especially unbleached pulps, to achieve a sizing effect similar to rosin and alum.

One method of making the pulp hydrophobic is to use a synthetic size, for example, stearic acid anhydride. A size emulsion may be made according to the art disclosed in U. S. Pat. No. 3,445,330. The size emulsion is added to a pulp slurry to about 0.3 to 1.0 percent of anhydride by weight of oven dried fiber slurry and stirred. The pulp slurry is dewatered and pressed to a consistency of 20-60 percent fiber solids. The pulp is then fluffed and dried, such as by flash drying by hot gases. For easy storage and shipping the sized, dried fibrous product may be compressed into bales. By the term "dried" it is meant the pulp contains less than 25 percent by weight of water. Before using, it is desirable to shred or reffluff the baled pulp to expose the sorbing surfaces and reduce the bulk density.

The practice of this invention is more clearly illustrated in the following examples.

EXAMPLE 1

This example illustrates the sizing of pulp for use in adsorbing oil. Two hundred grams (O.D.) samples, some of bleached hardwood pulp and others of unbleached pine pulp were diluted to 0.5 percent by weight slurry. A size emulsion of stearic acid anhydride

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made according to U. S. Pat. No. 3,445,330 was added to the pulp slurry at 25°C. After adding the size emulsion, stirring was continued for 1 minute. Then the water was drained from the slurry with a cotton bag and the pulp was pressed. After pressing the pulp was weighed for consistency and then fluffed with two passes through a Bauer single disk refiner using a devil tooth rotating plate. The fluffed pulp was dried in a Bowen laboratory spray dryer. The pulps were dried with either one or two passes through the dryer to simulate the commercial flash drying process which is used to produced baled pulps for market sales. The conditions for pulp samples are shown in Table 1.

TABLE I

Pulp	Bleached Hardwood	Unbleached Pine
Amount of size, %	1.0	1.0
Sizing consistency, %	0.5	0.5
pH in size slurry	6.1	7.3
Consistency after pressing	25.0	35.0

Drying Conditions

Sample	Passes thru Dryer	Inlet Air Temp. °F.	Solids %
A	Bleached Hardwood	10	820
B	Bleached Hardwood	2	820
C	Bleached Hardwood	2	780
D	Un- bleached Pine	1	820
E	Un- bleached Pine	2	820
F	Un- bleached Pine	2	650
			490

Oil adsorption tests were conducted on the sized pulp samples. A measured amount of 10 grams of two types of oil [Corvus oil by Texaco or transmission fluid] were put on top of water in separate beakers. One gram pulp samples were added to each beaker. In the beaker the pulp samples floated on top of the water and sorbed all the oil. Both the bleached hardwood and unbleached pine performed equally well. Similar tests with dried pulps which were not sized indicated that these pulps do not have oil sorbing properties. The unsized pulps were quickly wetted with water, sunk and the oil layer remained floating on top of the water. This example indicates that when 1% size is used to size bleached hardwood or unbleached pine pulp, the pulp is able to sorb at least 10 parts oil per 1 part dried pulp.

EXAMPLE 2

This example compares pulps sized to various levels with unsized pulp and wheat straw. The synthetic size emulsion containing 23.48 grams per liter stearic acid anhydride was used to size samples of pine pulp at different levels. 100 grams (O.D.) samples of pulps were diluted to 20 liters, demineralized water and size emulsion were added. Stirring of the pulp continued for 1 minutes after addition. The pulp was then dewatered with a press and fluffed with two passes through Bauer single disk refiner. The sized pulps were oven dried at 105°C. The following levels of size were used and the samples tested for oil pick-up.

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TABLE II

Pulp No.	Sample	Size on Pulp, %	Consistency After Pressing %	Addition of Cor- vus oil to 1 gram sample (pulp on top of water pulp sunk and the added 10 ml. oil floated on top of water
1	Unbleached Pine Pulp	0	25.8	pulp floated but did not sorb all 10 ml. of oil
2	Unbleached Pine Pulp	0.2	23.0	pulp floated but did not sorb all 10 ml. of oil
3	Unbleached Pine Pulp	0.4	23.0	pulp floated but did not sorb all 10 ml. of oil
4	Unbleached Pine Pulp	0.6	20.6	pulp floated but did not sorb all 10 ml. of oil
5	Unbleached Pine Pulp	0.8	24.8	pulp floated and sorbed almost all 10 ml. of oil
6	Unbleached Pine Pulp	1.0	26.2	pulp floated and sorbed all 10 ml. of oil ± additional 10 ml.
7	Wheat Straw	0	—	Reported capacity of 5 ml. of oil per gram straw*

* Report of Batelle Northwest Institute to the American Petroleum Institute 1971.

These results show that the effectiveness of the sorbing capacity of the pulp increases as the size level is increased. Further, at 1 percent size, the dried product is superior in oil absorbing capacity to wheat straw.

EXAMPLE 3

This example illustrates the application of this invention to commercial grade pine pulp samples partially dewatered before sizing. Preparation of sized pulp with stearic acid anhydride was made in the same manner as Example 1, except that solid stearic anhydride was mixed into pulp after the first fluffing stage in disk refiner. Addition of the size at this process stage, i.e., after the excess water is removed by pressure, insures 100 percent retention of the size without special retention aids such as starch or other polymer and alum. The stearic acid anhydride was added in solid form at three levels, 0.5 percent, 1.0 percent and 2.0 percent on oven dry pulp (1.0, 2.0 and 4.0 Grams stearic acid anhydride per 200 grams O.D. pulp). Drying of the stearic acid anhydride sized pulps was made in a Bowen spray dryer. The results are shown in Table III.

TABLE III

Sample No.	Sizing Agent	Amount Size, % on O.D. Pulp	Solids Content After Fluffing %	Solids content after Drying, % 2-passes at 650°F.
1	No Size	0	47.9	92.2
2	Stearic Acid Anhydride	0.5	48.5	91.7
3	Stearic Acid Anhydride	1.0	48.3	92.2
4	Stearic Acid Anhydride	2.0	47.9	93.3

These sized pulp samples were tested for oil sorbing capacity. The stearic acid anhydride pulps sized at 1 percent and 2 percent sorbed at least 10 times their own weight.

EXAMPLE 4

This example illustrates the application of this invention to commercial grade pulp samples sized with an asphalt type emulsion size. Preparation of sized pulps with Bitusize B was made in the same manner as Example 2, except that an asphaltic size was mixed into the pulp after dewatering and fluffing. The asphaltic emul-

sion, Bitusize B, was added at levels of 5.0 percent and 10 percent on oven dry pulp. Drying of these sized pulps was made in a Bowen dryer. The results are shown in Table IV.

TABLE IV

Sample No.	Sizing Agent	Amount Size, % on O.D. Pulp	Solids Content After Fluffing, %	Solids Content after Drying, % 2-passes at 650°F.
1	No Size	0	47.9	92.2
2	Bitusize B	5.0	51.2	95.1
3	Bitusize B	10.0	49.9	95.7

These sized pulp samples were then tested for oil sorbing capacity. Both Bitusize treated pulps sorbed at least 10 times their own weight.

EXAMPLE 5

This example illustrates the application of this invention to commercial grade pulp samples sized with rosin or an asphaltic emulsion size wherein the size is added to a pulp slurry and alum is used to improve retention and to fix the size to the fibers, and to orient the molecules of the size such that the surface of the fibers becomes hydrophobic. Unbleached pine pulp was slurried in water at 3.0 percent consistency and the size and alum added as indicated below.

TABLE V

Sample No.	Sizing Agent	Amount of Size, % on O.D. Pulp	Amount of Alum, % on O.D. Pulp
1	Rosin	1	1.5
2	Rosin	5	6.8
3	Bitusize B	1	1.5
4	Bitusize B	5	3.8
5	None Added	0	1.5

All of the pulps produced in this example were capable of sorbing 10 ml. of oil per gram of pulp from the surface of water. Sample 5 illustrates that the unbleached pine pulp used in these trials contained enough natural sizes to give the desired water repelling and oil sorbing capacity when alum was added.

While the invention has been described and illustrated herein by references to various specific materials, procedures and example, it is understood that the invention is not restricted to the particular materials, combinations of materials, and procedures selected for that purpose. Numerous variations of such details can be employed, as will be appreciated by those skilled in the art.

What is claimed is:

1. A process for making a hydrophobic, oleophilic fibrous material which comprises, slurring a lignocellulose pulp, dewatering the slurry to a consistency of about 20-60 percent, and flash drying the fibrous material, wherein at least 0.05 percent of a sizing material is introduced to the pulp either before dewatering or after the initial dewatering but before the drying process.
2. The process of claim 1 wherein said fibrous material is wood pulp.
3. The process of claim 2 wherein said wood pulp contains at least 1.0% by weight sizing material.
4. The process of claim 2 wherein said pulp is resin and alum sized.
5. The process of claim 2 wherein said wood pulp is sized with stearic acid anhydride.
6. The process of claim 2 wherein said wood pulp is sized with a stearic acid anhydride emulsion.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,770,575 Dated November 6, 1973

Inventor(s) Frank J. Ball

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, Table II, Pulp No. 7, the "0" following "Wheat Straw", should be in the column under -- Size on Oven Dry Pulp, % --.

Claim 4, line 1, "resin" should read -- rosin --.

Signed and sealed this 9th day of April 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

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Commissioner of Patents