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METHOD OF REFINING SULFATE TURPENTINE

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This invention relates to the treatment of crude turpentine and more particularly to a process of deodorizing turpentines which are obtained as a by-product in the manufacture of cellulose according to the sulfate process, and also the development of a product of pleasing odor and of high quality.

A further object is the provision in a method of the character described of improved steps for eliminating the offensive and obnoxious odor otherwise arising from the presence of sulphur compound developed by the re-agents in the process.

To these and other ends the invention resides and certain improvements and combinations of parts all of which will be more fully described hereinafter.

In the ordinary method of manufacture sulphate pulp, the cellulose material to be treated (usually wood chips) together with the usual chemicals are placed in a digester and steam admitted until the pressure in the digester reaches 110–135 pounds with the consequent temperature within the digester from about 335 to 350° F. Heat is supplied to the cooking vessel or digester by direct supply of steam or by external heat; the cooking liquor is then circulated through the cooking vessel during the cooking operation. In the case of heat with indirect steam the cooking liquor is circulated through the digester and an outside heat exchanger. In the direct heat the steam furnishes circulation by turbulence within the digester. It is a common practice to relieve steam and other vapors generated in the digester during cooking operation. This removal is usually done as the pressure is being increased in the digester. Occasionally at the end of the cook, part of the steam is removed to partially relieve the pressure before the contents of the digester are blown. The steam which is drawn off at the times indicated carries with it vapors of turpentine and other volatile compounds liberated from the wood or woody material. These vapors are carried through a suitable condenser which condenses the water and oil vapors. The condensed vapors are led into a separating device where the condensed oil layer is removed and then sent to storage and the water layer sent to waste. The oil layer is known as crude sulphate wood turpentine.

Due to the presence of sodium sulphide in the cooking liquor a number of exceedingly malodorous sulphur compounds may be formed. Such compounds may include mercaptans, dimercaptans, thio-ethers, sulphoxides, sulphones, sulphinic acids, sulphonic acids, disulphides, thioaldahydes, thioketones, esters, amides and other complex sulphur or nonsulphur compounds. Some or all of these compounds may be present in the crude sulphate turpentine, imparting to it an exceedingly offensive odor, the removal of which presents the chief problem in producing sulphate wood turpentine of a pleasing and marketable odor.

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It has been found that this problem is efficiently solved by the present process which is a combination of chemical and other steps.

In accordance with one aspect of the present invention, crude sulphate turpentine refined by what may be termed a chemical extraction process employing a material such as kraft mill green liquor. The kraft pulp mill green liquor is substantially immiscible in crude sulphate turpentine but capable of dissolving, combining with or in some manner in removing odor producing bodies contained therein.

The process of the present invention includes intimately contacting the crude sulphate turpentine with kraft mill green liquor or its equivalent, permitting the mixture to separate into an upper layer composed of refined turpentine and a lower layer composed of substantially said green liquor and the odor producing bodies contained in the crude sulphate turpentine. The upper layer is withdrawn and subjected to further treatment as hereinafter more specifically set forth. The lower layer is withdrawn and sent to the kraft mill green liquor storage tank and may be used in the kraft process without detriment to such process.

In order to disclose the nature of the present invention still more clearly, an illustrative example will hereinafter be described. It should be clearly understood however, that this is done purely for the purpose of illustration and is not to be considered a limitation upon the spirit of the scope of this invention.

Example I.—About ten parts of crude sulphate turpentine is stirred with about five parts of kraft mill green liquor. The kraft mill green liquor is preferably added in several increments at a temperature of about 80 to about 100° F. for about ten minutes. The material is permitted to stand until the two layers separate. The lower layer consists of the green liquor and the odor producing bodies and this is withdrawn and may be returned to the kraft mill green liquor storage. The upper layer consisting of turpentine is treated with bleaching material in water such as calcium hypochlorite. The amount of available

chlorine required will vary from about 4 to about 12% of the weight of the turpentine. Suitable agitation is desirable for mixing of the turpentine and the calcium hypochlorite then is contacted for several hours with activated carbon. The activated carbon removes by absorption residual coloring matter in the turpentine. The result of the foregoing treatment is a mild odored turpentine ready for commercial use.

If desired, the turpentine obtained may be subjected to distillation. However, for commercial use the distillation step is not required.

The amount of treating liquor used in refining the crude sulphate turpentine is based primarily on the amount of sulphur compounds contained in the crude sulphate turpentine. As the sulphur compounds, particularly the mercaptans increase in the crude sulphate turpentine, the amount of treating liquor must be increased to obtain satisfactory results.

In the kraft or sulphate process of fiber liberation as heretofore described, the wood chips are heated under pressure inclosed digesters with an alkaline cooking liquor known as "white liquor." A typical white liquor contains

Sodium hydroxide	4.00 #/ cu. ft. as Na_2O
Sodium sulfide	2.17 #/ cu. ft. as Na_2O
Sodium carbonate	.93 #/ cu. ft. as Na_2O

The composition of the white liquor may vary with different woods and different cooking schedules etc. This liquor extracts the lignin and other non-cellulose constituents of the wood and is discharged from the digester at the end of the cook as a dark liquor known as "black liquor." In ordinary sulfate mill practice, the black liquor is concentrated and the black liquor is then burned or smelted in a furnace with the addition of sodium sulfate. The organic matter is burned out in the furnace and the inorganic constituents are recovered which are dissolved in water to form a make-up liquor known as "green liquor." The composition of green liquor is as follows:

Sodium sulfide	2.19 #/ cu. ft. as Na_2O
Sodium hydroxide	.32 #/ cu. ft. as Na_2O
Sodium carbonate	4.67 #/ cu. ft. as Na_2O

The composition of green liquor may vary from mill to mill. This green liquor is used as a base for making up supplies of white liquor for reuse in the digesters by causticizing it with lime.

An important feature of the invention resides in the use, as an odor extracting medium, of a solution containing the inorganic constituents normally found in the cycle of a kraft paper mill, that is one or more of the constituents of green liquor or white liquor. Such solutions can be withdrawn from the kraft mill cycle, and when the extraction is completed, the spent extracting liquor can be returned to the mill cycle.

It will be observed by one skilled in the art

that the foregoing specification is subject to modifications and such variations as come within the spirit of the invention are intended to be included in the appended claims.

What is claimed is:

1. A method of obtaining commercially usable turpentine which comprises, separating crude turpentine from vapors removed from a kraft cooking process, withdrawing green liquor from the kraft mill cycle and mixing such withdrawn liquor with the crude sulphate turpentine, permitting the mixture to stand until separated into two layers, removing the lower layer and returning it to the kraft mill cycle and withdrawing the top layer as refined sulphate turpentine.

2. A method of refining crude sulphate turpentine to obtain commercially usable turpentine which comprises, extracting from said crude sulphate turpentine odor producing compounds with an aqueous solution containing sodium hydroxide, sodium carbonate and sodium sulfide.

3. A method of refining sulphate turpentine containing malodorous compounds which comprises, treating said turpentine with an aqueous solution containing green liquor as prepared in a kraft paper mill.

4. A method of refining crude sulphate turpentine containing malodorous compounds which comprises, adding green liquor at a temperature of about 80 to about 100° F. to the crude sulphate turpentine, permitting the mixture to stand until separated into two layers, removing the upper layer of turpentine, adding calcium hypochlorite containing from about 4% to about 12% of available chlorine based upon the weight of the turpentine; and thereafter contacting the turpentine with activated carbon.

5. A method of refining sulphate turpentine containing malodorous compounds which comprises, treating said turpentine with an aqueous solution containing sodium hydroxide, sodium carbonate and sodium sulfide, withdrawing the turpentine and agitating the turpentine while mixing calcium hypochlorite solution therewith; and thereafter contacting the turpentine with activated carbon to absorb residual coloring matter in the treated turpentine.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,493,454	Jobson	May 6, 1924
1,938,693	Gillespie et al.	Dec. 12, 1933
2,283,067	Jennings	May 12, 1942

FOREIGN PATENTS

Number	Country	Date
23,467	Great Britain	1910