IDENTIFICATION AND REMOVAL OF ODOR BODIES IN CRUDE SULFATE TURPENTINE

By

CHIN-GUNG HSU

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University of Shanghai
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THESIS AND ABSTRACT APPROVED:

Henry P. Johnston
Thesis Adviser

Tom E. Moore
Faculty Representative

D. C. McIntosh
Dean of the Graduate School

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TABLE OF CONTENTS

Page

3. Experimental

INTRODUCTION

Sulfate turpentine is one of the by-products obtained from the sulfate paper pulping process. Knoesel (1) was the first man who made a thorough study of optimum conditions for reclaiming crude sulfate turpentine. He found that as steam was fed into the digester, the air came out of the opened relief valve in the top of the digester, and the time when the pressure reached one-half atmosphere, the turpentine began to come off. The vapors were condensed in a coil.

Now one of the modern systems in the United States for turpentine condensation and separation is that marketed by the Foster-Wheeler Corporation (2). In this method, an initial pressure of 110 pounds is built up in the digester, and the vapors are relieved through a cyclone separator to remove pulp particles and entrained liquor. The relief gases next pass into a special surface condenser then through a loop seal into a tank where the water and turpentine automatically separate and flow off, turpentine going to a storage vessel.

The yield of crude sulfate turpentine is primarily dependent upon the species of wood processed and the ratio of heart wood to sap wood. Halse and Dedichen (3) report 1 to 1.5 Kg. of turpentine per ton of pulp from spruce cooked by the sulfate process and up to 10 Kg. per ton of pulp when pine is used. Rodowski (4) reports 2.5 gallons of turpentine per ton of pulp as being obtained by an American mill. An average recovery of 2.5 to 5 gallons of turpentine per ton of pulp is reported by a number of investigators. Weissner (5) gives the following data:

TABLE I

YIELD OF SULFATE TURPENTINE

Wood Used	Raw Turpentine (Kg./t. pulp)
Spruce	1.4--1.9
Pine	9.6--12.1
Fir	11

According to the statistical reports of the Technical Association of the Pulp and Paper Industry (6), the United States produced 7,496,000 short tons of sulfate pulp in 1950. Granting a recovery of 3.5 gallons per ton, there should be available annually about 26,236,000 gallons of this turpentine. Therefore in the total turpentine production, this figure occupies an important part.

Purified sulfate turpentine (7) is a colorless liquid of characteristic pleasant odor, and contains 90 per cent alpha and beta pinene and not more than 1 per cent dipentene. It can be used not only in paints and varnishes (7), but also in the manufacturing of terpin hydrates, terpineol, synthetic camphor and other chemicals (8). The reason that sulfate turpentine has not been all recovered and used widely is due to its difficulty in refining. Crude oil has a strongly held odor which can hardly be removed. Sometimes a bad odor is regenerated during the distillation of crude oil after certain treatment. The aim of this work is to study the odorous impurities and possible methods of deodorizing crude sulfate turpentine.

HISTORICAL DISCUSSION

The odorous impurities in crude sulfate turpentine have been studied from 1907. Knoesel (1) mentioned that when the Leagen mill converted from the soda to the sulfate process in 1884; the remarkable change from the comparatively mild odor of the soda turpentine to that of the sulfate turpentine was the cause of serious dissatisfaction on the part of the customers. Klason and Person (9) pointed out that the most of the odor was due to the presence of allyl and methyl mercaptans and sulfides. Klason (10) later also stated that the methyl mercaptan is auto-oxidized in the presence of turpentine into methyl disulfide. He also proved that the lignin of pines contains methyloxy compounds ($ROCH_3$) which at the high temperature of the digester react with alkali and alkaline sulfur compounds to form first CH_3OH, then CH_3SH, and CH_3SCH_3.

$$ROCH_3 + NaOH \longrightarrow RONa + CH_3OH$$
$$ROCH_3 + NaSH \longrightarrow RONa + CH_3SH$$
$$CH_3SH + NaOH \longrightarrow H_2O + CH_3SNa$$
$$ROCH_3 + CH_3SNa \longrightarrow RONa + CH_3SCH_3$$

Postovski and Plusmin (11) attributed the odor to methyl mercaptan and methyl sulfide.

By fractional distillation of oily condensate from digester relief, Bergstroem and Fagerlind (12) found the main constituents were turpentine and methyl sulfide. Klason (10) also stated that the fraction of the crude oil distilling below 100° C. consisted chiefly of dimethyl sulfide and the fraction distilling between 100° and 150° C. contained dimethyl disulfide. Falk (13) gave the following table based on a metric ton of cellulose obtained from pine.

TABLE II

COMPOSITION OF OILY CONDENSATE

Material	Yield in G.
Mercaptan	62
Dimethyl sulfide	927
Dimethyl disulfide	103
Oil of turpentine	487
Distillation residue	721

In 1939, Dudley and Dalla Vale (14) stated that the turpentine contains odors of dimethyl sulfide, ethyl mercaptan and other sulfur compounds.

As to the purification and removal of the impurities in the crude sulfate turpentine, many investigations have been made. Bergstroem (15) indicated that by redistillation of crude sulfate oil, the malodorous products may be eliminated and the purified oil is then equal in quality to the natural oil of the wood. However, Klason (10) did not agree with these findings and found that distillation does not completely remove the bad odors coming from sulfur compounds, and that chemical treatment was necessary. He also mentioned that dimethyl disulfide boils at 117° C. only 40° lower than the oil of turpentine itself, so that its elimination by fractional distillation was difficult.

Postovski and Plusmin (11), in their investigation and purification of sulfate turpentine, found that the crude oil may be readily purified of compounds which gave precipitates with mercury salts (mercaptans and sulfides) by distillation in a current of steam. The first 15 per cent of this distillate contained 86 per cent of these sulfur compounds, and if 50 per cent of the oil was distilled, only 2 per cent of the sulfur compounds remained.

The use of sulfuric acid for purification of sulfate turpentine was described by Klason and Person (9). They stated that such impurities were not attacked by caustic alkali and were only partially attacked by compounds of the heavy metals, but it was found that impurities are completely decomposed by sulfuric acid. Treatment with 5-10 per cent of its weight of 50 per cent sulfuric acid was found to be the most satisfactory method. They also mentioned that the use of concentrated sulfuric acid was barred. It not only removes the sulfur bodies, but also resinifies the oil of turpentine with evolution of much heat.

Oxidizing agents had also been used in the purification and removal of the odor of the crude turpentine. Among these, bleaching powder was the most used one. But Postovski and Plusmin (11) found that the product contained only 30 per cent of pinene, the remainder of the pinene having been oxidized. The specific gravity of the oil increased from the original value of 0.861 to 0.9621. So they preferred to remove most of the sulfur compounds by partial distillation and to eliminate the remaining impurities with a dilute hypochlorite wash. Other powerful oxidizing compounds also have been applied, such as sodium peroxide (16), sodium percarbonate, perborate, persulfate (17) and nitrous gases (18), but none of these were found to be perfect. Most of oils after treatment with these compounds, will give off odor during the redistillation.

Kalb (19) mentioned that heating the sulfate turpentine with alkali hydroxide or alcoholic alkaline solutions in mixture with particles of soda lime or alkali metals, formed readily volatile sulfur compounds which could be driven off. This was followed by distillation and, if necessary for further odor improvement, by aeration or treatment with salts such as calcium chloride, sodium chloride and copper sulfate. With the same principle, Jenning (20) patented a method which consisted of heating the crude turpentine with an aqueous solution of caustic soda and lime, without substantially vaporizing the turpentine itself, to effect substantial removal of impurities from the turpentine, separating the aqueous solution from turpentine and thereafter steam distilling the turpentine and recovering a purified distillate.

Investigators have tried furan derivatives (21), ethylene diamine (22), ultraviolet irradiation (23), metal salts--such as lead acetate (10), copper chloride, iron chloride and zinc chloride (23)--and different absorbents like fullers earth, silica gel, bone black (24) and sawdust (11). Although the results were fairly well defined, none were satisfactory deodorizers of the oil.

EXPERIMENTAL

I. ANALYTICAL METHODS

Elementary Analysis. The sodium fusion method was selected for carrying out the elementary analysis. Sulfur, nitrogen and halogen tests were performed by shaking the treated stock solution from sodium fusion with lead acetate, ferrous sulfate-ferric chloride and silver chloride solution respectively. The presence of these elements were shown by the formation of black lead sulfide, blue ferric ferrocyanide and silver halide precipitates.

Sulfur Content. The most common method for the sulfur analysis is the peroxide bomb method. However, this method is limited by the fact that the weight of the oil sample should not exceed 0.3 g. which, in the case of the sample containing less than 0.5 per cent sulfur, gives less than 1.5 mg. sulfur in the fusion mixture and thereby tends to reduce the accuracy of the determination. The Parr oxygen bomb also cannot go very far. For that reason, the lamp method was selected with the procedure as follows:

1. Apparatus. The apparatus consists of a lamp, chimney, absorber and spray trap. Apparatus used here were all according to A. S. T. M. specification (25) except the absorber and spray trap. The absorber was half longer in height and the spray trap was substituted by a long curved tube.

2. Chemicals.

a. Sodium carbonate solution -- It was prepared by dissolving exactly 3.306 g. of c.p. grade sodium carbonate in one liter of distilled water.

b. Hydrochloric acid solution -- It was prepared by pouring 5.05 ml. of c.p. grade conc. hydrochloric acid (sp. gr. 1.185) into a one liter volumetric flask and adding distilled water to the mark. Ten ml. of this solution were checked and neutralized 10 ml. of the sodium carbonate solution.

c. Methyl orange solution -- It was prepared by dissolving 0.004 g. of methyl orange in 1 liter of distilled water.

3. Procedure. Pass two strands of new cotton wicking through the wick tube so that they are not twisted but are parallel in the wick tube. Pour into the clean dry lamp about 15 ml. alcohol-oil solution (50% alcohol by weight) or sulfur free alcohol (for blank test) and insert the cork containing the wick tube. After the wick has become saturated with the oil, adjust the wick height with a pair of sharp scissors. Weigh the oil and lamp assembly to the nearest 0.0001 g. Meantime thoroughly rinse out the absorber with distilled water and put into it exactly 10 ml. of the sodium carbonate solution from an accurate pipette and then dilute the solution with 10 ml. of distilled water. Rinse out the chimney and the suction tube (instead of spray trap) with distilled water. Dry the chimney and connect both to the absorber by using corks.

After all are set, apply gentle suction to both absorbers; light the oil lamp and place it in position under the chimney so that the top of wick tube extends into the chimney not more than 1 or 2 mm. above the edge. Adjust the suction so that a steady flame 12 to 18 mm. in height and free from smoke is obtained. The apparatus is protected from drafts. After burning the oil about 1 to 1-1/2 hours, extinguish the flame and stop the suction. Weigh the oil lamp immediately to the nearest 0.0001 g. and determine half of the difference, the weight of oil consumed. Disconnect the suction tube and chimney and wash them thoroughly with the methyl orange solution using a wash bottle with a very fine jet and collecting the washings in the absorber. Use approximately 35 ml. of the solution for washing. Carefully titrate the faintly yellow solution with the hydrochloric acid solution. During titration, carefully agitate the contents of the absorber by using a suitable rubber syringe bulb. As the end point is approached, draw the liquid back and forth between the bulbs after each addition of acid, agitating as before. When the permanent pink color appears, the end point has been reached. Read and record the volume of hydrochloric acid solution used.

The sulfur content in percentage is then calculated by the following equation:

$$\text{Sulfur } \% = \frac{\text{ml. of HCl for blank - ml. of HCl for sample}}{\text{g. of oil burned x 10}}$$

<u>Mercaptan</u>. According to literature (26), making the mercuric salt with mercuric chloride was the best method for identifying mercaptans. But here, by simple fractional distillation, mercaptan could not be separated from sulfide which also would form complex salts with mercuric chloride. And due to the small quantity, the mercaptan could not be purified by first treating with sodium hydroxide then regenerating with the action of acid upon the sodium salt. The tests used here were

1. Sodium nitroprusside test -- Upon passing the mercaptan gas or shaking the mercaptan solution with 2 ml. one per cent sodium nitroprusside solution and three drops of 10 per cent sodium hydroxide, a red color will develop. This cannot be regarded as specific test of mercaptan because

some other compound like hydrogen sulfide will give the same coloration with sodium nitroprusside.

2. Lead acetate test -- An aqueous solution of lead acetate (20%) is added to the alcoholic solution of mercaptan or often the mercaptan gas can be directly passed into the lead acetate solution. After a few minutes, yellow lead mercaptide precipitates out. The crystals are washed with alcohol by decantation then thoroughly on the filter and finally dried in a desiccator.

3. Two-four-dinitrochlorobenzene test -- Thirty ml. of alcoholic mercaptan solution are mixed with an aqueous solution of sodium hydroxide (0.4 g. in 3 ml. of alcohol) and 2,4-dinitrochlorobenzene (2 g.) in alcohol (10 ml.). The mixture is heated in water-bath during 10 min. and the solution filtered while still hot. The thioether will separate on cooling as gold yellow needles.

Sulfide. It was confirmed by making its derivatives, mercuric chloride complex compound and sulfone. The procedures for these preparations were

1. Making mercuric chloride complex -- To sulfide solution a 10 per cent alcoholic mercuric chloride solution is added drop by drop until no more white precipitate is formed. The white crystals are filtered out and recrystallized from alcohol. The final product is dried in a desiccator.

2. Preparation of sulfone -- The sulfide is dissolved in glacial acetic acid. The solution is treated with a 50 per cent excess of potassium permanganate, dissolved in 30 times its weight of water, to form the sulfone. The potassium permanganate is added with shaking as fast as it was decolorized. When all the potassium permanganate had been added, the

excess was removed by treating with a solution of sulfurous acid at room temperature, avoiding an excess of this reagent. In most cases, the sulfone occurs in the form of a colorless precipitate at this point. If not at this point, 2 or 3 volumes of cracked ice are added. The sulfone is filtered, dried and recrystallized from alcohol.

3. Special test for methyl sulfide -- Methyl sulfide differs from other sulfides, as it will react with mercurous chloride in the presence of water. A little white mercurous chloride powder is first added to the test sulfide solution, then 2 drops of water are added. In case of methyl sulfide, gray mercury quickly settles out.

Disulfide. The methods used here were

1. Making mercuric chloride complex -- To the test solution, add a sufficient quantity of saturated alcoholic or aqueous mercuric chloride solution. Allow the mixture to stand over night and filter out the crystals. Dry them in desiccator to prepare for a melting point determination.

2. Preparation of mercaptan -- Disulfide solution is first mixed with a calculated quantity of glacial acetic acid and zinc dust. Then this mixture is refluxed gently for 3 hours. The excess of zinc and acetic acid are removed by filtration and washing with water. The reduced solution is finally subjected to distillation. Any mercaptan formed, is confirmed with lead acetate or mercuric chloride tests. From the melting point of lead salt or the mercuric salt, disulfide can be identified.

II. QUANTITATIVE ANALYSIS OF SULFUR COMPOUNDS

The method used here was developed by Faragher, Morrell and Monroe (27).

Elementary Sulfur. Elementary sulfur was determined by shaking 200 ml.

crude oil with metallic mercury and filtering off the mercury sulfide. The percentage of elementary sulfur was calculated from the difference between the lamp determination before the treatment with mercury and after the treatment. It was 0.0728 per cent.

Mercaptan. One hundred fifty ml. of oil after removing elementary sulfur was shaken with 75 ml. of alcoholic plumbite solution made by mixing equal volumes of 95 per cent alcohol and an aqueous solution of sodium plumbite. The aqueous solution was made by saturating a 20 to 25 per cent solution of sodium hydroxide with lead monoxide and filtering off the excess of lead oxide. The oil was shaken with the alcoholic plumbite solution until it is sweet to the doctor test. The lead mercaptides were removed by the alcoholic plumbite solution. The treated oil was then washed with water and dried. The percentage of mercaptan sulfur was obtained by subtracting the percentage of sulfur in the oil after treatment from that before treatment. The value found here was 0.1280 per cent.

Disulfide. The oil (100 ml.) free from elementary sulfur and mercaptans was then refluxed with glacial acetic acid (100 ml.) and zinc dust (15 g.). After refluxing, the oil was washed with water to remove acetic acid and then treated with the alcoholic plumbite solution (50 ml.) to remove the mercaptan produced from the reaction. The percentage of disulfide sulfur was calculated from the difference -- 0.0108 per cent.

Sulfide. Oil from the determination of disulfide was then shaken with solid mercurous nitrate which will form an insoluble complex with sulfide, $R_2S \cdot HgNO_3$. After 10-15 minutes this mixture was filtered and a lamp determination was made. The difference here was 0.0609 per cent.

The sulfur remaining after all of the foregoing operations was 0.0107 per cent. This was residual sulfur which, according to Faragher, Morrell and Monroe (27), was represented by thiophene. However the final oil, even the crude oil gave no typical reaction of thiophene. So its presence was doubtful and the final value may be experimental error.

The whole analysis can be summarized as in table III.

TABLE III

QUANTITATIVE ANALYSIS OF SULFUR COMPOUNDS

			S	Sulfur %		
Oil	Treatment	Observations	Cpd.	Before	After	Diff.
Crude	Shake with mercury.	Some black particles cover the surface of the mercury.	S	0.2832	0.2104	0.0728
After above treatment	Shake with alcoholic sodium plumbite.	Alcohol layer turns to yellow and cloudy.	-SH	0.2104	0.0824	0.1280
After above treatment	1. Reflux with zinc and glacial acetic acid about three hours. 2. Shake with alcoholic sodium plumbite.	Oil smells worse than original, and turns the alcoholic solution to yellow.	-SS-	0.0824	0.0716	0.0108
After above treatment	Shake with solid mercurous nitrate	Yellow solid turns to gray	-S-	0.0716	0.0107	0.0609

III. PRELIMINARY EXAMINATION

The crude sulfate turpentine was obtained from West Virginia Pulp and Paper Company, Charleston plant, Charleston, South Carolina. It was a light yellow oil having an offensive odor. An elementary analysis showed the presence of sulfur and the absence of nitrogen and halogen. The sulfur content was 0.2832 per cent. The oil had a specific gravity 0.8661 (15.5/15.5°) and a refractive index 1.4695 (20°C.).

Upon distillation, bubbling started at about 34°C. and the first drop of distillate came out at 44°C. The temperature rose during the distillation along 92-130°C. The oil, about 76 per cent of the original volume, was distilled out from 155 to 161°C. By smelling the distillates obtained, the unpleasant odor was shown to be concentrated in the low boiling fractions. Also the sulfur analysis (lamp method) indicated that the fractions below 150°C. contained more sulfur than those above that temperature.

TABLE IV

FRACTIONAL DISTILLATION OF CRUDE OIL

Fractions °C.	Volume ml.	Odor (a)	Sulfur Content %
Crude	100	**	0.2832
34---43	gas	*****	47.50
44---70	0.4	****	3.60
71---100	0.7	****	
101---120	0.3	***	3.52
121---130	0.3	***	
131---150	2.0	***	
151---153	1.3	***	0.94
153---155	2.9	**	
155---156	10.9	**	0.0312
156	10.1	**	0.0302
157	12.9	**	
158	10.1	**	
159	20.2	**	0.0150
160	4.0	*	
161	8.1	*	0.0138
162	2.9	*	
163	1.0	*	
164	1.0	*	
165	0.9	*	
166	1.0	*	
167	1.0	*	
168	0.9	*	
169	1.6	*	
170 & up	5.6	*	

(a) Note: **** standard sniff test for crude oil.

IV. ANALYSIS OF FRACTIONS

Fraction 1 (34-43°C.). This fraction containing disagreeable gases, turned wet lead acetate paper to yellow and changed the color of sodium nitroprusside solution to red. These results indicated the presence of mercaptan. The gases were soluble in alcohol. This alcoholic solution gave a white plate like crystalline precipitate with 10 per cent alcoholic mercuric chloride solution, also immediately turned the white mercurous chloride and yellow mercurous nitrate to gray. So these compounds were shown to be low molecular weight members of mercaptans and sulfides.

For the identification of mercaptan, the alcoholic solution of this fraction was treated both with alcoholic 2,4-dinitrochlorobenzene and aqueous lead acetate in order to obtain respectively the sulfide of 2,4-dinitrobenzene and lead mercaptide. The first method failed, perhaps due to the quantity of the mercaptan being too small, so could not produce golden crystals. The product from the second method was a very lustrous yellow plate-like crystal which melted at 135°C. According to the literature (28), it was impossible to get a constant melting point for lead mercaptide by recrystallization, and also it was indicated that the melting point rises with increasing numbers of carbon atoms. So the ethyl mercaptan was proved in the gas.

TABLE V

MELTING POINT OF ALKYL MERCAPTIDE (29)

	Lead Salts	Mercuric Salts
Methyl	--- °C.	175 °C.
Ethyl	150	76
n-Propyl	96	72
n-Butyl	81	86

Faragher, Morrell and Comay (30) have shown that only methyl sulfide precipitates mercury from mercurous chloride in the presence of water. Other alkyl sulfides seemed to have no action on this mercurous salt even in the presence of water. Therefore the sulfide in this gas was methyl sulfide. For further identification of methyl sulfide, the oxidation method was used. Thirty ml. of alcoholic solution of this fraction and 10 ml. of glacial acetic acid were mixed. This solution was then treated with excess potassium permanganate, dissolved in 30 times its weight of water. The excess was removed by treating with a solution of sulfurous acid until decolorized. Needle crystals were precipitated out over night. The melting point of this sulfone was determined as 110°C. or very near to that of methyl sulfone 109°C. (31).

When the alcoholic solution of this fraction was treated with a 10 per cent alcoholic mercuric chloride solution, white crystals were formed which melted at 150-3°C. This phenomenon did not indicate a single definite compound, because mercuric chloride could form addition compounds with both ethyl mercaptan and methyl sulfide, $(EtSHgCl)_2 \cdot 2HgCl_2$ and Me_2SHgCl_2. Both addition compounds have a melting point about 150°C. (32).

The gas coming from the distillation of crude oil, previously treated with dilute sodium hydroxide, showed no reaction with aqueous lead acetate solution, yet formed white crystals (m.p. 151°C.) with 10 per cent alcoholic mercuric chloride solution. It indicated the presence of methyl sulfide. At the same time, the presence of ethyl mercaptan was indicated.

The sulfur content of the gas which had been absorbed in alcohol was determined to be 47.50 per cent.

Fraction 2 (43-100°C.). The sulfur content of this fraction was 3.60 per cent. After careful redistillation, two sub-fractions were obtained 43-70° and 71-100° C. Both gave no reaction with aqueous lead acetate solution. However, white plate-like crystals were immediately precipitated on addition of alcoholic mercuric chloride solution to these fractions. Their melting points were different. The precipitate from first sub-fraction (43-70°) melted at 149-151°C. But the second one seemed to decompose at high temperature. About half of the crystals sublimed at 115-125°C. and left a gray solid which melted at 145°C.

The oxidation test of these fractions, as described under fraction 1, gave needle crystals (m.p. 110°C.) in the first sub-fraction, but failed in the second sub-fraction.

Phillips (33) gives 151°C. as the melting point of $2Me_2S \cdot 3HgCl_2$, while for $Et_2S \cdot HgCl_2$ Faragher, Morrell and Comay (30) record 77°C. and 119°C. from different recrystallizing solvents (alcohol and acetone).

From these results, it was clear that no ethyl sulfide was present. The sulfur compound in this fraction was largely methyl sulfide.

<u>Fraction 3 (100-150°C.)</u>. Most of this fraction was distilled out above 130°C. From the lamp method analysis, the sulfur content was determined as 3.52 per cent. A white precipitate slowly formed during the addition of mercuric chloride solution. The color of this precipitate changed graduately to pink. After standing for twelve hours, plate-like crystals were formed. The melting point of these crystals was 140-5°C., very close to the value 141°C. which was reported by Blackburn and Challenger (34) as $MeSHgCl \cdot xHgCl_2$ from Me_2S_2 and aqueous mercuric chloride solution.

For further proof of the existence of methyl disulfide, reduction methods (27) were used. The crude oil was first treated with mercury and alcoholic plumbite in order to remove elementary sulfur and mercaptans, then 50 ml. of this oil were mixed with 50 ml. of glacial acid. The mixture was refluxed for 3 hours with 10 g. of zinc dust under a long water cooled condenser. The excess of zinc was removed by filtration. The sample containing the acetic acid was washed with water in a separatory funnel. The acetic acid passed into the water layer and the oil remained in the upper layer. The oil was washed several times with water and then distilled over a small flame. The gas distilling first, gave a yellow precipitate with aqueous lead acetate solution, but it disappeared shortly after filtering and exposure to air. The residue left on the filter paper was black, like lead sulfide. The melting point for lead ethyl mercaptide was 150°C., but no melting point of lead methyl mercaptide has been reported. This was due perhaps to its unstability.

The reason for the change of color of the addition compound with mercuric chloride may be explained by the formation of complex salt $HgS \cdot HgCl_2$. Jolibois and Bouvier (35) mention that only HgS, black, and $2HgS \cdot HgCl_2$, white, exist as definite compounds. The composition of the intermediates, yellow red brown precipitates, varies proportionally to the content of the liquid in mercuric chloride. And HgS comes perhaps from the reaction between mercuric salt and elementary sulfur present in the fraction.

<u>Fraction 4 (150-155°C.)</u>. From sulfur analysis, this fraction contained only 0.94 per cent sulfur, which was much lower than the other three. Mercuric chloride and the reduction test gave the same results as the fraction 3 but less in quantity. The sulfur compound in this fraction was considered as the carry-over residue from the preceding fraction.

V. DEODORIFICATION

Four salts, mercuric chloride, mercurous nitrate, cupuric sulfate and cuprous chloride, were first tried for removal of odor bodies in the oil. A ten per cent alcoholic mercuric chloride solution was dropped into the crude oil until no further precipitate was formed. The precipitate was removed and the oil distilled. To two other flasks of crude oil (100 ml. in each), one gram of mercurous nitrate and cuprous chloride powder were added separately. After standing over night, the oils were recovered by filtration and distilled. In the fourth case, the oil was shaken with a saturated aqueous solution of cupric sulfate, and left over night. The treated oil was then removed with a separatory funnel and subjected to distillation.

By comparing the above treatments, mercuric chloride and mercurous nitrate removed the odor quite rapidly, but the unpleasant odor regenerated during the redistillation of the treated oil. The other two salts were capable of removing a part of the bad odor, but the oil still gave an obnoxious odor after treatment. It seemed that most mercaptan and sulfide had been removed. The disulfide and elementary sulfur were still present. This was confirmed upon distillation as the first drop in all cases came out at 85-90°C.

TABLE VI

RESULTS FROM PRECIPITATION

	Odor		
Reagent Used	After treatment	During distillation	Observations
10% alc.$HgCl_2$	*	*	White ppt. graduately turning to pink.
Solid $HgNO_3$	-	*	Yellow solid changes to gray particles.
Solid CuCl	**	**	Oil color changes to yellowish green
Sat.Aqu.$CuSO_4$	**	**	Yellowish green scum appears on the boundary

Note: Crude oil **** is used in this work to compare the degree of odor.

In an attempt to completely eliminate disulfide, a reduction method was used. Alcoholic sodium ethylate was chosen as a reducing agent and was prepared by adding 2 g. metallic sodium to 10 ml. absolute ethyl alcohol. During the refluxing of crude oil with alcoholic sodium ethylate, a small amount of bad odor gas (like hydrogen sulfide) escaped, which turned wet lead acetate paper to black. The color of the oil first changed to orange and finally to brown. After refluxing 3 hours, the oil still had a bad odor, but not so strong as before.

In reducing with metallic sodium, the same result was obtained as with sodium ethylate. The silvery metallic sodium changed to a dark brown substance.

Various oxidation methods were tested as follows:

1. Hydrogen peroxide -- Fifty ml. crude oil were first dissolved in an equal volume of glacial acetic acid in a 250 ml. three-neck flask fitted with a thermometer, stirrer and dropping funnel. The flask was immersed in an ice-water bath and stirred until the temperature of the mixture fell to 5°C. Superoxol, dissolved in an equal volume of glacial acetic acid, was added slowly from the dropping funnel with constant stirring. The progress of the oxidation was noted from time to time by testing with starch-iodide paper and the temperature was kept at 5° all the time. After the reaction mixture showed a positive starch-iodine test, one ml. more of hydrogen peroxide solution was added and stirring continued for 4 hours. Finally the reaction mixture was brought to room temperature, the oil separated and washed with water.

2. Bleaching powder -- Fifty ml. of a 10 per cent bleaching solution was shaken with 50 ml. of crude oil for 2 hours. The treated oil was then separated and distilled.

3. Chlorine -- One hundred ml. of crude oil were mixed with 25 ml. of glacial acetic acid and 25 ml. of water. Chlorine gas was then passed into the solution at a slow rate for about half an hour. The reaction flask was cooled by water in order to maintain it at about room temperature. At the end of the reaction, the oil was separated from the acid layer and washed with water.

4. Sodium peroxide -- One gram of sodium peroxide was refluxed with 100 ml. of crude oil under a small flame. The pale yellow sodium peroxide powder slowly turned to dark brown. After refluxing one hour, the oil was clarified by filtration and tested.

5. Air -- A 250 ml. two-neck flask, in which 100 ml. of crude oil had been added, was heated in a water bath with a condenser and an air bubbling tube. The speed of air bubbling into the reaction flask was rather slow, about 2-3 bubbles per second. This aeration was kept under reflux for 1 hour and then the oil was taken out and tested. During the aeration, the odorous gas coming out of the condenser was collected in alcohol. This gas turned lead acetate solution to yellow.

6. Ferric chloride -- One hundred ml. of crude oil were heated for 1 hour with 60 ml. of 40 per cent ferric chloride solution in a refluxing system. After heating, the oil was distilled.

7. Sulfur -- Eight tenths gram of sulfur powder was refluxed with 100 ml. of crude oil for 1/2, 1, and 2 hours. The results from those cases seemed alike.

8. Phosphorous pentoxide -- The oil was shaken with phosphorous pentoxide powder and allowed to stand over night. The color of phosphorous pentoxide and oil all changed to reddish brown, which meant that polymerization occurred.

9. Phosphoric acid -- During the shaking of 85 per cent phosphoric acid with crude oil, polymerization appeared slowly. The color of the resinous material was dark brown.

10. Sulfuric acid -- Concentrated and 50 per cent sulfuric acid were tested. Four drops of concentrated sulfuric acid was the maximum quantity which could be added to 100 ml. of crude oil. At this point, the oil turned to pink color. If one more drop of acid was added, a black resinous substance appeared. When 10 per cent by volume of 50 per cent sulfuric acid was shaken with crude oil, the acid later turned to pink with little odor improvement.

11. Two, four-dinitrobenzene -- Oxidation with 2,4-dinitrobenzene and alkali was also tested. Water and alcohol served as mediums. The amount of materials used in treating 100 ml. of crude oil were 2,4-dinitrobenzene 2 g., sodium hydroxide 0.2 g., and 100 ml. of medium. The procedure was to shake the mixture and let it stand for 24 hours. Refluxing the mixture for 1 hour was also tried. The results seemed just the same.

Among all these treatments, hydrogen peroxide showed the best result. Sodium peroxide, air, ferric chloride, sulfur, phosphorous pentoxide, dilute sulfuric acid and alkaline 2,4-dinitrobenzene indicated only a little effect on sulfur compounds; while bleaching powder, chlorine gas reacted with pinene and the odor was only slightly improved.

Although concentrated sulfuric and phosphoric acids oxidized and dissolved some sulfur compounds, they also polymerized the oil and produced resinous substances.

TABLE VII

RESULTS FROM OXIDATION

Reagent Used	Odor After Treatment	Remarks
Crude oil	****	
Hydrogen peroxide	-	No odor is regenerated during reditn.
Bleaching powder	*	
Cl_2	*	Treated in water and HAc medium.
Na_2O_2	*	
Air	*	
$FeCl_3$	**	
Sulfur	**	
P_2O_5	**	
conc. H_3PO_4	*	Polymerization appears slowly.
50% H_2SO_4	*	
conc. H_2SO_4	-	Polymerization occurs.
2,4-dinitrobenzene	**	Treated in an alkaline medium.

In searching for a simpler deodorizing method, electrolytic oxidation-reduction was carried out. The procedure of this method could be summarized as follows: one hundred forty ml. of reaction medium were placed in an electrolytic cell, and 70 ml. of crude oil were added also. The electrolytic cell was constructed with a 250 ml. beaker, a stirrer and two electrodes. The size of electrodes was 2 x 5 cm., and they were set about 5 cm. apart. A storage battery was used as a source of electricity and connected with the two electrodes. Between battery and cell, a variable resistance and a voltmeter were jointed in series and parallel respectively with the circuit in order to control and measure the applied voltage. The stirrer was turned on immediately as the current passed in. After the electrolytic reaction had been carried out 1 hour, the current was disconnected. The reaction mixture was removed from the cell, set over night and separated. During the distillation of treated oil, no liquid came out until 110°C. Here two boiling fractions(100-155°, 155-157°) were collected and compared, either by smell or test with alcoholic mercuric chloride solution. The experimental conditions were

TABLE VIII

ELECTROLYTIC EXPERIMENTAL CONDITIONS

Area of electrodes	10 cm^2.
Volume of oil used	70 ml.
Volume of medium used	140 ml.
Current	D.C. 5.8v.
Temperature	20° C.
Time	1 Hr.

From many trials, copper electrodes and tap water solvent gave the best results. The comparative results from different cases were as shown in table IX and X.

TABLE IX

COPPER ELECTRODES AND DIFFERENT MEDIUMS

Medium	pH	Cl%	Odor of treated oil
4 drops conc. H_2SO_4 in 140 ml. water	2.00		***
5 drops Cl_2 water in 140 ml. tap water	6.35	0.0039	*
1.5 g. $CaCl_2$ in 140 ml. water	6.65	0.60	**
3 g. NH_4Ac in 140 ml. water	7.15		**
1 g. NH_4Cl in 140 ml. water (a)	8.90	0.44	-
140 ml. tap water	8.90	0.0027	-
1 g. Na_2SO_4 in 140 ml. water (b)	8.90		*
3 g. NaAc in 140 ml. water	9.20		**
1 g. NaCl in 140 ml. water	9.65	0.41	*
0.2 g. NaOH in 140 ml. water	10.05		**
2 g. Bleaching powder in 140 ml. water	12.20	0.75	**
70 ml. glacial HAc with 70 ml. water			*
70 ml. alcohol with 70 ml. tap water			**

(a) pH adjusted by adding conc. NH_4OH
(b) pH adjusted by adding conc. H_2SO_4

TABLE X

TAP WATER MEDIUM AND DIFFERENT ELECTRODES

Cathode Material	Anode Material	Odor of oil after treatment
Cu	Cu	-
Cu	C	*
Hg	Cu	*
Cu	Hg	**
Zn	Cu	**

During the electrolytic oxidation-reduction, black particles appeared on the cathode surface. The copper anode became dark red. In using NH_4Cl or Na_2SO_4 in the medium, the copper anode went into solution very quickly. The color of the oil changed from yellow to yellowish green. Upon distillation of the treated oil, no liquid came out under 110°C. In all cases, the distillate collected from 110°-155°C. gave a white precipitate turning to pink with alcoholic mercuric chloride solution on standing. But only a trace of precipitate was formed after using copper electrodes and tap water medium.

Alternating current also was tried, but the results were not satisfactory. The odor diminished as the applied voltage was increased as shown in Table XI.

TABLE XI

RESULTS WITH ALTERNATING CURRENT

Electrodes' material	Medium	Voltage	Odor of treated oil
Cu	Tap water	6	***
Cu	Tap water	15	***
Cu	Tap water	30	**
Cu	Tap water	60	*
Cu	Tap water	90	*

DISCUSSION

The odor bodies of the crude sulfate turpentine were found to be ethyl mercaptan, methyl sulfide, and methyl disulfide. The major offensive odor is due to the ethyl mercaptan. According to literature (36) the odor of sulphydryl compounds is very strong and one part in fifty billion of ethyl mercaptan in air may be detected by odor. While the odors of methyl sulfide and methyl disulfide are not so objectionable as those of sulphydryl compounds.

From analysis of the fractions, the presence of ethyl mercaptan and methyl sulfide are very definite. Although disulfide was thought to be present, the existence of methyl disulfide was not definitely shown. The disulfide might be ethyl disulfide formed by the reaction of ethyl mercaptan and elementary sulfur. Due to the minute quantity contained in crude oil, no good method could be found for identification. From the melting point of the mercuric complex compound and the unstability of the lead salt produced by the action of lead acetate upon the reduced material, the methyl disulfide was considered a possibility.

Just after this work was done, a new discovery of sulfur compound in sulfate turpentine was reported in the latest copy of The Paper Industry (37). It mentions that Bruun, Hafnor and Sorensen in the Norweigian Institute of Technology had found a toxic sulfur compound, $CH_3SCH_2CH_2SCH_3$, in the high boiling fraction of crude sulfate turpentine. They did not isolate this sulfur compound, but obtained its oxidation product, $CH_3SOCH_2CH_2SOCH_3$, in alpha and beta-pinene fraction, appearing as a small deposite of crystals together with an oil. They also stated that this oxidation product is very sparingly soluble in acetone and melts at 156-8°C.

In considering the production and the usefulness of crude turpentine, it was found to be a very valuable raw material. So the problem of refining had already been studied. Precipitants, oxidizing agents, absorbents and solvents had been tried by many investigators. Although there are many patents around the world about the removal of the odor substances; a successful method for industrial use has not been discovered. Most of the old methods recommended by previous workers cannot completely remove the odor bodies, either leaving a little obnoxious odor in the treated oil or are too expensive. Some of them were tried here.

In general, the odor of the oil after treatment with salts is much improved but is not completely removed. In the case of copper salts, either cupric or cuprous, only eliminate a part of the odor. It is perhaps due to the inactivity of copper salts toward sulfide and disulfide. They only act upon mercaptans to form as $Cu(SR)_2$. Mercury salts act very well but a part of the odor regenerates during the distillation. It may be explained that mercury salts cannot completely react with sulfur compounds, especially with disulfide, because the odor reappears in the high boiling fraction after distillation. This incomplete reaction of mercury salts and sulfur compounds may also be due to the destruction of complexs by hydrogen sulfide. And hydrogen sulfide is produced by the reaction of elementary sulfur and hydrogen chloride formed during the reaction of mercuric chloride and sulfur compounds.

As we know, sulfur compounds are very easily oxidized. The products, sulfonic acid and sulfone, are readily dissolved in water and separated from the oil. But in the case of using sulfur, ferric chloride or phosphorous pentoxide as an oxidizing agent, only mercaptans are oxidized to disulfide. On the other hand, the main constituents of sulfate turpentine, alpha and beta pinene, can also be easily oxidized into terpineol by hydrogen peroxide, chlorine and other powerful oxidizing agents. So oxidation method must be carried out with care. Here a very low temperature, 5°C. has been chosen as reaction temperature. Under this condition, pinene will be oxidized only very slightly by hydrogen peroxide. According to Engler (38), the rate of the oxidation of pinene increases with temperature and is very slow at 0°C. However the procedure is rather complicated and not suitable for industrial use.

Electrolytic oxidation-reduction method gave very good result for the refining of crude oil. The important reaction involved appeared to be the oxidation of sulfur compounds rather than reduction. It was found that the electrode material must be one which has a very small hydrogen overvoltage. Copper electrodes served very well in this work. The nature of medium also influenced the result. From a series of experiments it was shown that the pH value of the medium was very critical. A successful result was obtained only at a pH of 8.9 and a chloride concentration less than 0.44 per cent. With either more or less than these values gave less than complete removal. This phenomenon may be explained by assuming that the chloride served as a catalyst. Without its help, the electrolytic reaction did not go to completion. And also as the oxidation of sulfur compounds is very easy in an acid solution, so a medium with a high pH value cannot be used, because it will hinder the oxidation. On the other hand, the oxidation products from sulfide and disulfide are sulfonic acid and disulfone which can easily react with a base and be taken out. Therefore the medium cannot go too far on the acid side. It can be shown (table XII) that acidity of medium after reaction increases on standing with the treated oil.

TABLE XII

CHANGE OF pH OF MEDIUM ON STANDING

Time	pH
Before reaction	8.9 (tap water)
After reaction	6.7
1 day after reaction	5.9
2 days after reaction	5.5
3 days after reaction	5.3
4 days after reaction	5.1
5 days after reaction	4.8
10 days after reaction	3.2

So a standing period is necessary before further refining such as distillation.

In table XI, we see that the odor of the oil is improved with the increase of the applied voltage. This shows that a high current density is required in this electrolytic reaction. Due to the low flash point of turpentine, a high voltage current has not been tried. Perhaps a higher voltage alternating current will also give a good result, but excessive heat development makes it inadvisable.

SUMMARY

The odor bodies of the crude sulfate turpentine oil were studied. They were due largely to the presence of sulfur compounds. Almost all of them were concentrated in the low boiling fraction, but were not separated out from turpentine according to their boiling points. They were identified as ethyl mercaptan, methyl sulfide, methyl disulfide and elementary sulfur.

In removal of sulfur compounds from crude sulfate turpentine, it cannot be done completely by treating with heavy metal salts or simply by distillation. Oxidation with hydrogen peroxide in cold acetic acid medium gives a good result, but its procedure is rather complicated and expensive.

Electrolytic oxidation-reduction with different electrodes were tried. The copper electrodes proved to be the best. Various medium like water, alcohol and acetic acid were studied. It was shown that a slightly basic water solution with a little chloride content gave excellent results. Furthermore, on varying the pH value and chloride content of the water medium, it was found that tap water (pH = 8.9) gave the best result. Sometimes a little odor will reappear during the distillation which immediately follows the electrolytic treatment. But when the distillation is performed after allowing the treated oil to stand for 4-5 days, the sulfur compounds were undetectable by smell in the refined oil. Even on addition of alcoholic mercuric chloride solution, no reaction was apparent.

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NAME OF AUTHOR: Chih-Gung Hsu

THESIS ADVISER: Dr. H. P. Johnston

The content and form have been checked and approved by the author and thesis adviser.

NAME OF TYPIST: Harold A. Coonrad