Refining of Low Temperature Cresol No. 1

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The low temperature cresol No. 1 has an offensive smell and a strong tendency of spontaneous coloration. According to Funakubo et al.[1], coloration of tar-acid oil occurs in the presence of acetic and formic acids, and more rapidly when the oil is exposed to the sunlight or contains a trace of iron together with acetic and formic acids. It has been stated by Lunge[2] that coloration of phenol has its origin in ferric benzoate formed from benzoic acid in the tar-acid oil and iron from distilling equipments, and he referred to indene as another source. According to Ueda et al.[3], coloration of tar-acid oil is caused chiefly by pyrrol, and in the case of low-temperature tar, catechol also partakes of its cause. Jaeger[4] said that coloration of tar occurs chiefly by oxygen in the air and basic oil promotes the coloration.

Egloff et al.[5] reports that spontaneous coloration of gasoline is due to free sulfur and alkyl disulfides, and when both are present, remarkable coloration takes place. According to Suzuki et al.[6], an offensive smell of low temperature tar is due to thiophenols.

The investigations of impurities in the coal tar products have become the topics of interest in recent years. However, only a little literature has been published on the inquiries of impurities in the low temperature cresol No. 1 which may cause the offensive smell and coloration.

The present paper is the report on the researches of the impurities which may deteriorate the quality of low temperature cresol No. 1, and on the suitable method for removing them.

This study revealed about thirty substances as impurities in the low temperature cresol No. 1, including those which have not been certified in coal tar up to the present. Several of them showed remarkable spontaneous coloration and strong peculiar smells, and these substances together with other unstable materials, which may cause the disgusting smell and coloration, were successfully removed by oxidation and active-clay treatment. The impurities in this refined cresol were investigated, and it was found that most of them were removed.

The author has reported the results of his inspections of the impurities in the low temperature cresol No. 1 in the Journal of the Chem. Soc. of Japan, Ind. Chem. Sec. from part 1 to 7, and in this paper the results have been summarized and discussed further.

Experimental Results

(1) Preparation and Properties of Low Temperature Cresol No. 1—At the Nitrogen Factory of Ube Industries, Ltd., the low temperature cresol No. 1 is prepared by the way shown in Tables I and II. The low temperature cresol No. 1 has an offensive smell and a dark brown color, and its specific gravity is 1.036 at 24°C. Engler's distillation curve is shown in Fig. 1.

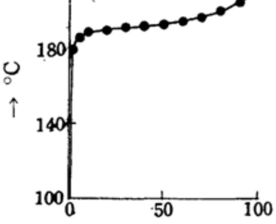

Fig. 1. Engler's distillation curve.

Immediately after distillation, the low temperature cresol No. 1 is a colorless and transparent oil, but gradually it begins to color on storage in the open air, and finally becomes an opaque black brown oil. In a dark place, however, its color turns only a light yellowish red in thirty days after distillation, which is lighter than the coloration caused by leaving the distillate

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[1] E. Funakubo and G. Kawasaki, unpublished data.

[2] G. Lunge, "Coal-Tar and Ammonia" Part I, Gurney and Jackson, London, (1916), p. 266.

[3] T. Ueda and H. Matsuda, Japanese Patent No. 199, 897.

[4] A. Jaeger, *Brenn. Chem.*, **1**, 257 (1923).

[5] G. Egloff, J. C. Morrell, W. L. Benedict and C. Wirth, U. O. P. Booklet No. 35, Universal Oil products Company, Chicago, (1938).

[6] M. Suzuki, F. Kitahara and M. Koga, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (*Kogyo Kagaku Zassi*), **55**, 28 (1952).

TABLE I

SEPARATION OF CRUDE ACID OIL FROM LOW-TEMPERATURE TAR

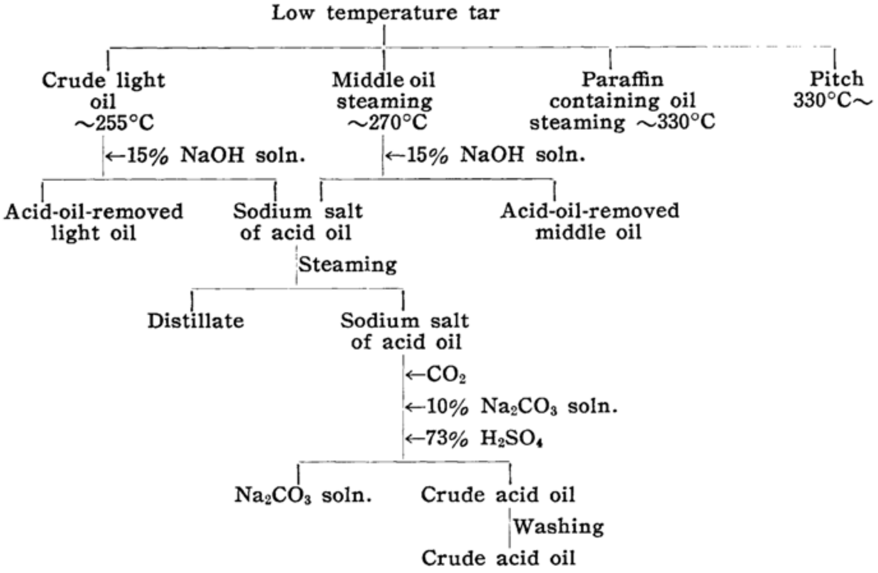
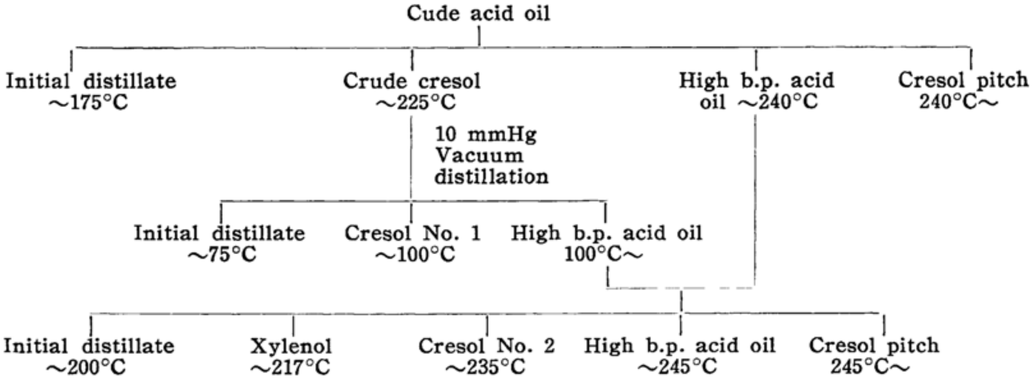


TABLE II

PREPARATION OF LOW TEMPERATURE CRESOL No. 1



in the air for one day. When the low temperature cresol No. 1. is distilled under a stream of nitrogen or carbon dioxide, and the distillate is stored in a glass bottle, containing nitrogen or carbon dioxide, the coloration does not develop in thirty days after distillation, and the distillate remains colorless and transparent just as it is immediate after distillation. On the other hand, the low temperature cresol No. 1 absorbs a considerable amount of oxygen, and the coloration is nearly proportional to the amount of absorbed oxygen⁷⁾.

In the case of lack of either light or oxygen, the low temperature cresol No. 1 is stable enough against coloration. So, it is clear that the remarkable coloration occurs only when both light and oxygen are present.

According to Amemiya et al.⁸⁾, for example, the components of low temperature cresol No. 1 are: 23 weight% of phenol, 8 of *o*-cresol, 22 of *m*-cresol, 11 of *p*-cresol and 31 of xylenols and the higher homologs, (including 5% operation loss). The impurities in the low temperature cresol No. 1 were determined by the method listed in Tables III and IV. The composition was 0.217 volume % of strong acid oil, 0.367 of weak acid oil, 0.733 of neutral oil and 0.033 of basic oil, and the total impurities were 1.350 volume %. The 176~210°C fraction of normal acid oil obtained by removing these impurities from the low temperature cresol No. 1, did not color even when it was left in the open air⁹⁾, and had no more offensive smell. Thus it is indicated that the materials included in these impurities cause an offensive smell and spontaneous coloration.

(2) Identification of the Constituents of

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7) K. Yamada, ibid., **60**, 1319 (1957).

8) J. Amemiya, E. Tunetomi and T. Nagazawa, *J. Japan Tar Ind. Association*, **4**, 104 (1952).

9) K. Yamada, *J. Chem. Soc. Japan*, *Ind. Chem. Sec.*, (*Kogyo Kagaku Zassi*), **60**, 591 (1957).

10) K. Yamada, ibid., **60**, 921 (1957).

TABLE III

SEPARATION OF STRONG ACID OIL, NORMAL ACID OIL

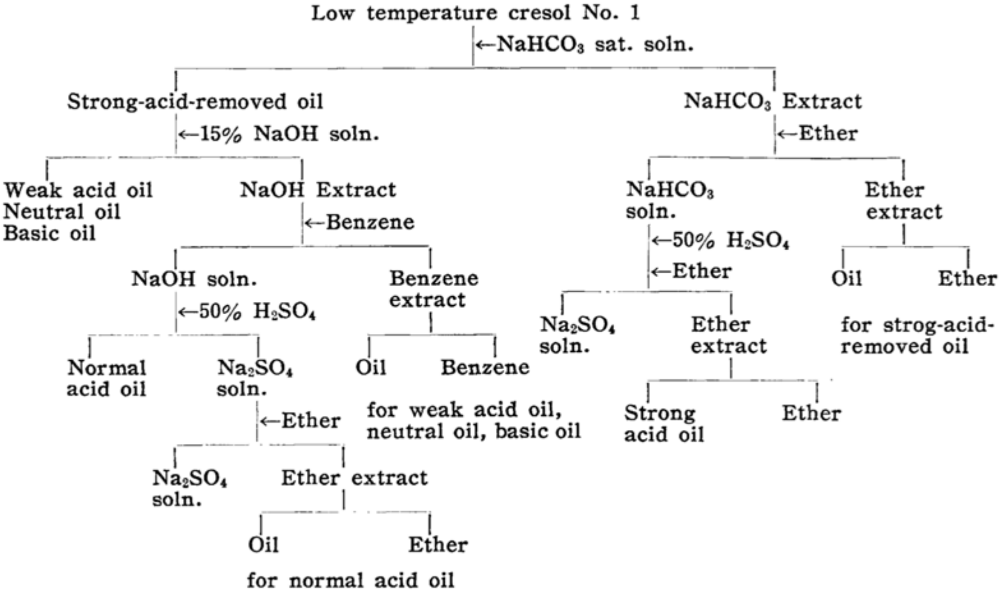

TABLE IV

SEPARATION OF WEAK ACID OIL, NEUTRAL OIL, BASIC OIL FROM BENZENE EXTRACT

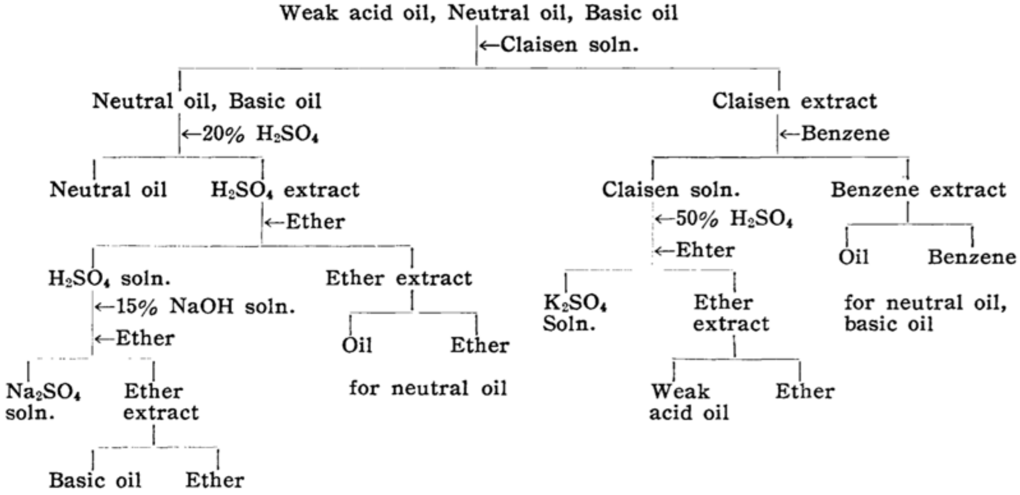

TABLE V

SULFUR CONTENT IN SEVERAL SAMPLES (wt. %)

Sample	(1) Low temperature cresol No. 1	(2) Lower boiling fraction	(3) Medium fraction	(4) Residue
Total S (A)	0.0427	0.0183	0.0160	0.0792
Hydrogen sulfide S	0.0003	0.0004	0.0001	0.0000
Elementary S	0.0070	0.0059	0.0054	0.0059
Mercaptan S	0.0061	0.0045	0.0036	0.0032
Disulfide S	0.0012	0.0010	0.0008	0.0010
Sulfide S	0.0004	0.0005	0.0004	0.0005
Thiophene S	0.0010	0.0005	0.0004	0.0010
Sum up (B)	0.0160	0.0128	0.0107	0.0116
Total S in Residue (A−B)	0.0267	0.0055	0.0053	0.0676
B/A	37.4	69.9	66.8	14.7

the Impurities.—*a*) *Strong Acid Oil.*—The distillation curve of the strong acid oil is similar to that of the low temperature cresol No. 1, but the former is contained chiefly in the lower boiling fraction of the low temperature cresol No. 1.[10] Strong acid oil has an offensive and stimulative smell like rancid butter.

Several acidic impurities such as propionic, *iso*-butyric, *n*-butyric, *iso*-valeric, *n*-valeric acids and catechol were detected in the strong acid oil by means of rectification, specific gravity, refractive index, neutralization value, bromine number, paper chromatography, melting point of the corresponding derivatives (amides), mixed-melting point test with the corresponding authentic samples, ultraviolet absorption spectra and infrared absorption spectra of each fraction[10].

The iodine number of the carboxylic acid fraction isolated by esterification, hydrolysis and extraction, was 110.2. On heating, the strong acid oil forms polymeric material; this fact suggests the presence of unsaturated acids.

b) *Weak Acid Oil.*—Weak acid oil in impurities was rectified, and the specific gravity, the refractive index, the boiling point, the average molecular weight and the hydroxyl value of each fraction were determined; furthermore qualitative test (ferric chloride test), melting-point test of the derivatives (phenoxy acetic acids) and mixed-melting point test with the corresponding authentic samples were also made. Upon these experiments, the presence of *p*-cresol, 2,4- and 2,5-dimethylphenols was noticed[11].

It seems that *p*-cresol, because of its small dissociation constant, intrudes into weak acid oil in the course of separation based on the said method. The rest of the components of the weak acid oil are supposed to be higher boiling phenols such as dimethylphenols, trimethylphenols, ethylphenols and methylethylphenols.

c) *Neutral Oil.*—The distillation curve of the neutral oil shows that fractions below 176°C, as well as fractions above 210°C and residue, occupy a considerable amount of the total distillate, and that medium fractions (176∼210°C) take a much smaller part, though this temperature range corresponds to the main fraction of the low temperature cresol No. 1[11].

So it is possible to say that a considerable amount of unstable materials which polymerize easily by heating, is included in the neutral oil. The neutral oil was rectified and the specific gravity, the refractive index, the sulfur content, the absorption loss by sulfuric acid and the iodine number of each fraction were determined. There was a great deal of absorption loss by both 80 and 98% sulfuric acid; especially the lower boiling fractions were absorbed more by 80% sulfuric acid, and showed high iodine numbers[11,12].

Every fraction was distinctly positive to silver mirror test and Schiff's reagent test. Carbonyl compounds in the neutral oil were investigated, through melting-point check of the derivatives (2,4-dinitrophenylhydrazones or semicarbazones) and mixed-melting point test with the corresponding authentic samples. Thus *n*-propyl methyl ketone, mesityl oxide, *n*-amyl methyl ketone, *iso*-butyl methyl ketone, *o*-hydroxybenzaldehyde, benzaldehyde, 4-methylcyclohexanone and acetophenone were detected in the neutral oil[11 12].

By the same research tests, aromatic hydrocarbons in the neutral oil were identified as *p*-xylene (*O*-aroyl tetrachlorobenzoic acid), mesitylene (*O*-aroyl benzoic acid) and naphthalene[11] (picrate).

d) *Basic Oil.*—Forty nine volume per cent of the basic oil runs out below 150°C and 71% below 176°C in contrast to the case of the low temperature cresol No. 1 which gives a little distillate below 176°C[13].

Through several tests as described in the previous sections and of derivatives (mercuric chloride complexes and picrates), 2-, 3-, 4-methylpyridines, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-dimethylpyridines, 4-ethylpyridine and 2,4,6-trimethylpyridine were identified in the basic oil[13].

e) *Sulfur Compounds.*—The low temperature cresol No. 1 contains 0.0427 weight % of sulfur. Concerning spontaneous coloration, each fraction of the low temperature cresol No. 1 and classified impurities were studied. On the other hand, sulfur content was measured in each sample. As a result it was found that the degree of coloration is nearly parallel to sulfur content[14]. Sulfur contents measured in conformity with their chemical forms are shown in Table V. Four samples were checked: (1) low temperature cresol No. 1, (2) its lower boiling fraction (15 volume %), (3) medium fraction (50%), (4) residue (33%) (water 1 %, loss 1%).

According to Table V, it is understood that all of them contain free sulfur and mercaptans as predominant constituents, alkyldisulfides as next, and a little of hydrogen sulfide, alkyl sulfides and thiophenes are also contained.

(3) Purification by Oxydation.—*a*) *Spontaneous Coloration of the Refined Cresol.*—As stated above, the coloration of the low temperature cresol No. 1 hardly ever occurs in the absence of oxygen, even if it is exposed to the sunlight. It absorbs a considerable amount of oxygen and the relation between coloration and absorbed oxygen is almost proportional. These facts led to the idea that the impurities which bring about spontaneous coloration by absorbing oxygen, are to be removed by the use of enough amount of oxidizing agent, followed by adsorption of the products on active clay.

As the oxidizing agent, potassium cyanoferrate or sodium bichromate was used. Adopting one of the oxidizing agents only, or active clay only, or both substances, purification by oxidation was carried out in several cases. The most preferable result was obtained when the low temperature cresol No. 1 was treated with 0.2% of potassium cyanoferrate together with 5% of

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[11] K. Yamada, ibid., **60**, 1314 (1957).

[12] K. Yamada, ibid., **61**, 269 (1958).

[13] K. Yamada, ibid., **60**, 1310 (1957).

[14] K. Yamada, ibid., **60**, 925 (1957).

active clay, and, after filtration, the distillate of 176~210°C (90 volume % of yield) was collected7). The product was named "Refined Cresol".

Hourly change of color was examined on four samples. They are: (1) above-mentioned refined cresol, (2) 176~210°C distillate of the low temperature cresol No. 1, (3) medium 50% of the distillate (25~75 volume %) of the first class *m*-cresol (97 % of this was distilled at 201~202°C), (4) 176~210°C distillate of the normal acid oil which was prepared by removing strong acid oil, weak acid oil, neutral oil and basic oil from the low temperature cresol No. 1.

Using spectrophotometer, transmissions at wave lengths 420, 470, 520, 580, 620 and 700 mμ were measured, and by their mean value, the degree of coloration was represented. Fig. 2 shows the results obtained when the samples were placed by the window to be exposed to the sunlight and Fig. 3 shows that obtained when they were exposed to the ultraviolet rays.

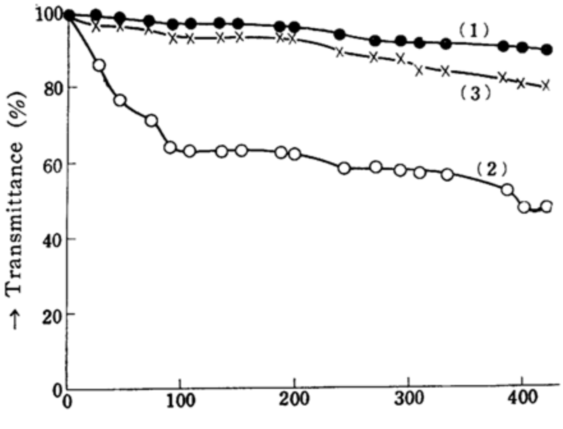

Fig. 2. Spontaneous coloration by the sunlight.
(1) ● Refined cresol
(2) ○ Low temperature cresol No. 1
(3) × *m*-cresol

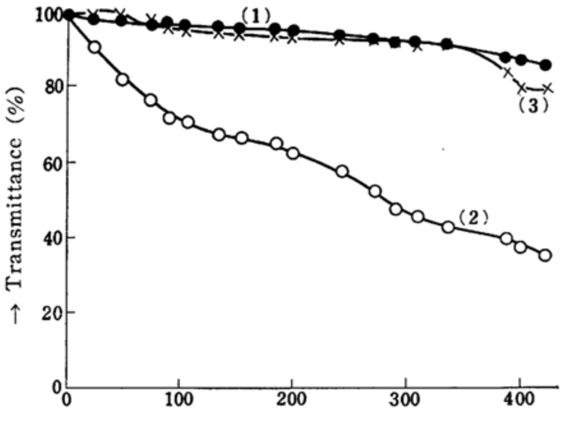

Fig. 3. Spontaneous coloration by the ultraviolet rays.
(1) ● Refined cresol
(2) ○ Low temperature cresol No. 1
(3) × *m*-cresol

As the refined cresol and the normal acid oil free from the impurities gave nearly equal results, the description of the latter was omitted.

Figs. 2 and 3 indicate that the coloration of the refined cresol advances very little. Therefore, most of the impurities which influence the spontaneous coloration of the low temperature cresol No. 1 seem to be eliminated by this operation.

TABLE VI

IMPURITIES IN THE REFINED CRESOL (vol. %)

	Low temperature cresol No. 1	Refined cresol
Strong acid oil	0.217	0.154
Normal acid oil	95.133	95.749
Weak acid oil	0.367	0.403
Neutral oil	0.733	0.411
Basic oil	0.033	0
Total impurities	1.350	0.968
Sum up	96.483	96.717
(Loss)	(3.517)	(3.283)

TABLE VII

SULFUR CONTENT IN THE REFINED CRESOL (wt. %)

Sample	Low temperature cresol No. 1	Refined cresol
Total S (A)	0.0427	0.0151
Hydrogen sulfide S	0.0003	0.0001
Elementary S	0.0070	0.0042
Mercaptan S	0.0061	0.0026
Disulfide S	0.0012	0.0007
Sulfide S	0.0004	0.0002
Thiophene S	0.0010	0.0005
Sum up (B)	0.0160	0.0083
Total S in Residue (A−B)	0.0267	0.0068
B/A	37.4	55.0

b) Impurities in the Refined Cresol.—Impurities and sulfur compounds in the refined cresol are shown in Tables VI and VII.

Results and Discussion

(1) Formation of the Impurities.—As shown in Tables I and II, sodium salts of the strong acid oil are formed by adding 15% sodium hydroxide solution to the crude light oil and the middle oil. When carbon dioxide is introduced to the sodium salts, normal acid oil is separated as an oil layer, but owing to weak acidity of carbon dioxide the sodium salts of the strong acid oil remain in the same form in aqueous layer and are rejected together with the waste liquor of the sodium carbonate.

A small amount of sodium salts of the

strong acid oil still remaining is removed by washing with 10% sodium carbonate aqueous solution, but a portion of the sodium salts remains in the crude acid oil. These sodium salts change to the strong acid oil at the time of 73% sulfuric acid washing, and they form strong acidic impurities in the normal acid oil.

Weak acid oil is accompanied by the normal acid oil as it has the same chemical properties except for possessing slightly higher boiling point than that of the normal acid oil.

Neutral oil which comes through dissolution or mixing into the sodium salts of the acid oil, is removed at the steaming of the sodium salt, but their portion remains through dissolution and become neutral impurities in the normal acid oil.

A typical composition of the crude light oil shown in Table I is 47.5 volume % of acid oil, 2.0 of basic oil and 50.5 of neutral oil; of this neutral oil, 12.2 and 46.3 volume% are the parts absorbed by 80 and 98% sulfuric acid respectively, so that 41.5 volume% of the neutral oil is the unabsorbed part by 98% sulfuric acid. On the other hand the typical composition of the oil (distillate in Table I) which has been distilled off by the steaming of the sodium salts of acid oil is 42% of acid oil, 11 of basic oil and 47 of neutral oil; the absorption diminutions of this neutral oil by 80 and 98% sulfuric acid are 51.5 and 44.0 % respectively. Thus the portion unabsorbed by 98% sulfuric acid is only 4.5%.

Neutral oil in the low temperature cresol No. 1 is also absorbed largely by 80 and 98% sulfuric acid, and the unabsorbed is about 2%. Therefore the neutral oil which enters into the sodium salt of the acid oil through dissolution or mingling, is such a peculiar oil as to be absorbed in 80 and 98% sulfuric acid.

Basic oil forms particular compounds with acid oil[15], and a large amount of the former is removed by sulfuric acid washing, but through dissolution its portion remains, similar to the case of the neutral oil, in the sodium salts of acid oil, forming the impurities in the normal acid oil.

On this account, not only by the above mentioned manufacturing process but also by the improved process where the sodium salts of acid oil are washed with benzene, more or less impurities, including weak acid, strong acid and neutral and even basic oil, get inevitably mixed with the low temperature cresol No. 1.

(2) **Decrease of the Impurities by Refining.**—As shown in Table VI the impurities in the refined cresol have considerably decreased in contrast to those in the low temperature cresol No. 1. According to a qualitative test the presence of catechol is indicated in the strong acid oil of the low temperature cresol No. 1, but not in the refined cresol. The iodine number of the strong acid oil in the low temperature cresol No. 1 and that of the strong acid oil in the refined cresol is 180.8 and 73.9 respectively. Diminution of iodine number seems to indicate the decrease of unsaturated acids, the content of the weak acid oil having scarcely changed.

The presence of carbonyl compounds is shown by a qualitative test in the neutral oil of the low temperature cresol No. 1, but not in the refined cresol. The iodine number of the neutral oil in the low temperature cresol No. 1 and that of the neutral oil in the refined cresol are 59.2 and 24.2 respectively, and this diminution seems to indicate the decrease of unsaturated compounds.

As to the neutral oil of the low temperature cresol No. 1 and that of the refined cresol, the absorption diminutions by 80% sulfuric acid are 24.0 and 9.4 volume % respectively; by 98% sulfuric acid they are 73.5 and 86.0%, unabsorbed part being 2.5 and 4.6%.

As the yield of the refined cresol is 90%, the decrease of the neutral oil contained in 100 cc. of the low temperature cresol No. 1 by this refining process is calculated as follows: the absorption diminution 0.176 cc. by 80% sulfuric acid is decreased to 0.035 cc., the absorption diminution 0.539 cc. by 98% sulfuric acid is decreased to 0.318 cc., and unabsorbed oil 0.018 cc. is decreased to 0.017 cc..

Since carbonyl compounds are well absorbed by 80% sulfuric acid and easily react with iodine, it may be said that carbonyl impurities are especially cut down by this refining process. Almost all basic oil is removed by this process. As shown in Table VII, the content of sulfur compounds decreases considerably by this purification.

Summary

Low temperature cresol No. 1 has an offensive smell, and its spontaneous

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[15] Y. Ohshima and K. Ishibashi, ibid., **29**, 445 (1925).

coloration is remarkable. It was treated with an oxidizing agent and active clay for the purpose of refining, and then washed with sodium bicarbonate solution in order to remove carboxylic acids which give a strong peculiar smell. Refined cresol which has no more offensive smell and shows a little spontaneous coloration, was obtained.

The impurities in the low temperature cresol No. 1 and in the refined cresol were measured, and it was found that in the refined cresol every impurity was decreased; especially unsaturated carboxylic acids, carbonyl compounds and basic oil were diminished. In the strong acid oil were detected, propionic, *iso*-butyric, *n*-butyric, *iso*-valeric, *n*-valeric acids and catechol, in the weak acid oil, *p*-cresol, 2, 4- and 2, 5-dimethylphenols, in the neutral oil, *n*-propyl methyl ketone, mesityl oxide, *n*-amyl methyl ketone, *iso*-butyl methyl ketone, *o*-hydroxybenzaldehyde, benzaldehyde, 4-methylcyclohexanone, acetophenone, *p*-xylene, mesitylene and naphthalene and in the basic oil, 2-, 3-, 4-methylpyridines, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-dimethylpyridines, 4-ethylpyridine and 2,4,6--trimethylpyridine, respectively.

Sulfur compounds were measured in accordance with chemical forms, and it was found that free sulfur and mercaptans are contained as the predominant components, and alkyl disulfides as the next; a little hydrogen sulfide, alkyl sulfides and thiophenes are also present.

Coal tar contains many components, and two hundred and eighty-two[16], or three hundred and ninety-four components[17] have already been reported in the literature of the subject.

But *n*-propyl methyl ketone, mesityl oxide, *n*-amyl methyl ketone, *iso*-butyl methyl ketone, *o*-hydroxybenzaldehyde, benzaldehyde and 4-methylcyclohexanone, that have been identified in this study, are not found in literature. Among those substances listed above, many have strong peculiar smell, and exhibit spontaneous coloration.

The refined cresol, which was treated with the oxidizing agent, active clay and sodium bicarbonate solution, scarcely has any offensive smell and exhibits only a slight spontaneous coloration. Measurement of the impurities in the refined cresol shows that almost all the above mentioned substances have been removed. Thus it is concluded that an offensive smell and spontaneous coloration of the low temperature cresol No. 1 arise, at least partially, from these substances.

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[16] O. Krubber, A. Raeithel and G. Grigoleit, *Erdöl und Kohle*, **8**, 637 (1955).

[17] The Coal Data Book (Loose-Leaf), Section A-4 "List of compounds identified in and isolated from coal tar", The Coal Tar Research Association, Oxford Road, Gomersal, Nr. Leeds. (1956).