physical methods; but it makes the fourth class, the composition of matter, look like the remnants of the shell-shot cathedral at Rheims, with patentability hanging on by an eyelash. It is not abolished—not all of it; just most of it. Some compositions will be patentable and some not—those whose pedigree is in any way tainted with the "chemical." A little chemistry will damn a thing quite as effectually as a great deal since courts will not draw distinctions between much and little, that being purely a "question of degree." The alibi of the guiltless inventor would have to be absolute, and there might be some difficulty of proving it in the absence of any universally accepted definition of "chemical." At present neither I nor anybody else can write an impeccable definition of the word, one which would stand fire in court. I do not even know, for example, whether dissolving sugar in water is a "chemical" process.

Shifting the anathema to "chemical compound" does not help any, since if a chemical compound is something resulting from chemical action (which is as good a definition as any) we come out the same hole we went in, with the additional burden of defining a "compound." In a general way I know what a compound is; we all do. It is a body composed of two or more elements united in definite proportions, which, however, is just as true of type metal as of aniline; or, for that matter, of any good uniform grade of cast iron.

I fear me that any attempt to sort out the chemical goats from the physical sheep in the composition of matter class would prove like the task of hunting polar bears in purgatory—"apt to be arduous in detail and disappointing in result." There are too many hybrids, goatish sheep and sheepish goats. It would be simpler to abolish the whole class at one fell whack. But I do not understand anybody wants to do this. So far as I understand, the chemist is the only chap it is meant to ostracize; and even he may escape if he does not have intelligence to know what is happening when he stews two things together.

Despite the present popularity of class legislation, being a hidebound Republican I do not like it; and as a chemist I object to being the class if the legislation is discriminatory against me. To deprive the chemist of his reward for his labor by taking away his "product" claim (whatever that "product" claim may be) is the same to him as depriving the machinist of his claim to his machine or the weaver to his new article in the way of a fabric. It is not good equity; and moreover it is not good sense. The object of the patent laws is to promote the progress of science and the useful arts, and that they have fulfilled their mission is beyond a peradventure. Why stop now and stop in a single science? For 125 years (to be exact, since Feb. 21, 1793) the chemist has been as much entitled to look forward for reward for what he did as anybody else; he read his title just as clear as did the machinist. Maybe I am biased, and very likely I am, but I can't, for the life of me, see wherein there is any legal or equitable difference between the standing of the chap who puts together an alkyl radical and an aryl radical to make a new drug or a new dye and the man who puts together levers and keys to make a new typewriter. That the product of one is sold in a bottle and the product of the other in a box is not material. Any argument that seeks to discriminate between them is as lop-sided as a crane; and I don't like being on the wrong side of the lop. It is at least as much an object to the public to encourage the chemist by patents as it is to encourage the machinist. Both are human and, commonly, poor, and neither is going to strain his ingenuity working nights unless he sees a patent ahead.

Running through all this "product patent" talk like a rotten streak in a mushy banana, is the idea that the chemist who creates a new drug or dye that becomes a public necessity as soon as its creation and existence are known to the public is guilty of creating public necessities to his own profit, and he ought to be discouraged; or if he won't be, then he should not be allowed to make the profit—which sounds like a curious piece of mental perversion, worthy of the gentleman who habitually stood on his head to peel the apple dumplings; but I am not gilding the lily any in reproducing it—far from it; I am merely condensing and Englishing certain actual arguments which have been made.

Washington, D. C.
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ORIGINAL PAPERS

SULFITE TURPENTINE

By A. W. Schorger
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During the recovery of the sulfur dioxide, in the manufacture of pulp by the sulfite process, a small amount of oil collects on the surface of the liquor in the separator and is known as sulfite turpentine. The oil varies in color from pale yellow to black and is frequently strongly impregnated with sulfur dioxide. Various mills have reported a recovery of 0.36 to 1.0 gal. of turpentine per ton of pulp. The species of wood employed in order of their importance are spruce, balsam, and hemlock. It has been reported that no oil is obtained from cooking hemlock.

The United States produced 1,027,000 tons of sulfite pulp in 1909 and Canada produced 470,948 tons in 1916. The present annual production in the two countries exceeds 1,500,000 tons. Granting a recovery of only 0.5 gal. per ton, there should be available annually about 750,000 gal. of this turpentine.

Klason[1] appears to have first called attention to

[1] *Ber.*, **33** (1900), 2343; cf. Kondakow and Schindelmeiser, *Chem.-Ztg.*, **30** (1906), 722; Kertesz, *Ibid.*, **40** (1916), 945.

the fact that the oil so obtained consists mainly of *p*-cymene and not of terpenes. The only reference found to the American oil is the statement of Herty and Graham[1] that sulfite turpentine consists mainly of cymene.

Cymene does not appear to be employed for any specific purpose. Verley[2] used it as the basis of a synthetic violet-like perfume. Dinesman[3] prepares thymol by a method unlikely to compete with the natural product; 2-Br-*p*-cymene is transformed to the 3- or 5-sulfonic acid. After elimination of the bromine by long heating in an autoclave with zinc dust and ammonium hydroxide, the cymene sulfonic acid is fused with potassium hydroxide to obtain thymol. In a previous paper[4] the writer has shown that by the action of aluminum chloride on cymene there are formed diisopropyl, benzene, toluene, *m*-xylene, and 1-methyl-3,5-diisopropyl benzene. The yield of toluene may amount to 40 per cent of the weight of the cymene, but this reaction cannot be employed economically except when very unusual prices prevail for toluene. Cymene also yields toluene by "cracking" processes.[5]

EXAMINATION OF THE OIL

Oils from three widely separated mills were distilled, using a 12-in. Hempel column with the following results:

Obtained from	Composition of Wood Per cent	Distillate					
		Up to 175° Per cent	175°–176° Per cent	176°–177° Per cent	177°–178° Per cent	178°–182° Per cent	Residue Per cent
Niagara, Wis..	Spruce 100	1.11	7.76	84.03	...	...	6.65
Erie, Pa......	Spruce 90 Balsam 10	7.66	15.18	39.60	33.66	...	3.74
Berlin, N. H..	Spruce 65 Balsam 35	0.43	2.57	22.00	19.00	35.00	8.81

The older oils when distilled usually give off considerable hydrogen sulfide. The distillation data indicate that the cymene content is greatest when all spruce is cooked.

IDENTIFICATION OF CYMENE

Characteristic of cymene is the barium salt $(C_{10}H_{13}\cdot SO_3)_2Ba\cdot 3H_2O$, sparingly soluble in water from which it crystallizes in shiny plates. The salt is best prepared as follows: To 50 g. of cymene in a flask are added 100 g. of fuming H_2SO_4 (10 per cent free SO_3). Shaking develops considerable heat and the solution is complete in about 10 min. The liquid is cooled, poured into a separating funnel, and about one-third of its volume of cold water added. On rotating the funnel carefully two layers are formed, the upper consisting of cymene sulfonic acid, and the lower of dilute sulfuric acid free from sulfonic acid. The cymene sulfonic acid should be dissolved in about 5 liters of boiling water, neutralized with barium carbonate, and the $BaSO_4$ filtered off. After removal of the salt of the 2-sulfonic acid, the filtrate contains the salts of the 3-sulfonic acid and disulfonic acid that can be separated with alcohol.[6] The yields of the three

salts from 50 g. of cymene were 79.9 g., 14.6 g., and 4.2 g., respectively.

When 35.4 g. of the anhydrous barium salt of the 2-sulfonic acid were heated with an equal weight of PCl_5 and the amide formed by heating with ammonia in the ordinary way, the yield of the cymene sulfamide was 18.93 g. (70.7 per cent of theoretical). The amide, recrystallized from water, melted at 114°.

The cymene was also oxidized to *p*-oxyisopropyl benzoic acid, m. p. 155°. As good results are obtained when only half of the amount of $KMnO_4$ given by Wallach[1] is used. This method is somewhat tedious and the yields are poor.

Cymene has been found to react readily with chlorosulfonic acid and when an approximately pure cymene is present this offers a superior means of identification. With the terpenes chlorosulfonic acid reacts with explosive violence. An equal volume of chlorosulfonic acid is gradually added, with constant shaking, to the cymene. The mass foams considerably, but the reaction soon completes itself with only a slight rise of temperature. The chlorosulfonic acid is separated by pouring into a separating funnel containing water, extracted with ether, and the ether extract washed with water to remove inorganic acids. After evaporation of the solvent the cymene chlorosulfonic acid is transformed to the sulfamide by heating with concentrated ammonia on the steam bath. The sulfamide is recrystallized from hot water, using a little animal charcoal. The method is rapid and the yields are excellent.

SULFAMIDE OF *p*-OXYISOPROPYLBENZOIC ACID—Ten grams of cymene sulfamide were oxidized by heating on the steam bath with 30 g. of potassium permanganate in 2 liters of water. The manganese sludge was filtered off, the filtrate evaporated to dryness and extracted with hot 95 per cent alcohol. The alcohol was evaporated and the residue extracted with hot commercial absolute alcohol. On cooling, the potassium salt of *p*-oxyisopropylbenzoic acid sulfamide was deposited as warty masses. The salt was dried at 110° for 48 hrs. and the potassium content determined as follows:

0.4950 g. salt gave 0.1403 g. K_2SO_4.

Calculated for $C_3H_6(OH).C_6H_3 < ^{SO_2.NH_2}_{COOK}$: K = 13.18. Found: K = 13.13.

CARVACROL FROM CYMENE

The annual importation of thymol has been about 6000 lbs.[2] In their physiological and antiseptic properties thymol and carvacrol appear to be very similar. A number of iodine compounds,[3] such as "aristol" and "annidalin," prepared from thymol, are reputed to possess very strong antiseptic properties. A similar compound,[4] "iodocrol," prepared from carvacrol, has been made in this country for several years.

The 2-sulfonic acid of cymene can be easily prepared, but the fusion with alkali as carried out on a

[1] THIS JOURNAL, **6** (1914), 803.
[2] German Patent 101,128 (1897).
[3] German Patent 125,097 (1901).
[4] *J. Am. Chem. Soc.*, **39** (1917), 2671.
[5] Rittman, British Patent 13,100, September 13, 1915.
[6] Claus, *Ber.*, **14** (1881), 2140.

[1] *Ann.*, **264** (1910), 10.
[2] Hood, U. S. Department of Agriculture, *Bulletin* **372.**
[3] Messinger and Vortmann, *Ber.*, **22** (1889), 2316; **23** (1890), 2754; Bayer & Co., German Patent 49,739.
[4] U. S. Patent 561,531 (1906); cf. Bayer & Co., German Patent 53,752 (1889).

small scale gave very poor yields of carvacrol. It is very probable, however, that satisfactory yields could be obtained from larger apparatus capable of more careful control.

CARVACROL—The calcium and barium salts of cymene sulfonic acid were made in the manner described above. The calcium salt is much more soluble than the barium. The sodium salt was prepared by decomposing a weighed amount of the barium salt with sodium carbonate in aqueous solution and evaporating to dryness after filtering off the barium carbonate.

The fusion was carried out by placing the sulfonic acid salt in a nickel dish on a sand bath and adding the alkali dissolved in a minimum amount of water, and gradually raising the temperature of the fused mass to about 300°, with constant stirring. This temperature should not be exceeded. The melt was dissolved in water, acidified, and distilled with steam. The carvacrol was extracted with ether and weighed after evaporation of the solvent. The yields of carvacrol are given in the following table:

YIELDS OF CARVACROL FROM CYMENE SULFONIC ACID

Fusion No.	SALT Kind	Wt. Grams	ALKALI Kind	Wt. Grams	Temp. of Fusion	CARVACROL Yield Gms.	% Theoretical
1	$(C_{10}H_{13}.SO_3)_2Ca.2H_2O$	10.00	KOH	30	300°	2.45	41.0
2	$(C_{10}H_{13}.SO_3)_2Ca.2H_2O$	10.00	K_2CO_3	30	300°	0	....
3	$(C_{10}H_{13}.SO_3)_2.Ba.3H_2O$	10.00	NaOH	30	350°	0	....
4	$C_{10}H_{13}.SO_3Na$	7.64	KOH	30	300°	0.61	8.0
5	$C_{10}H_{13}.SO_3Na$	7.64	NaOH	30	350°	0	....
6	$(C_{10}H_{13}.SO_3)_2Ca.2H_2O$	10.00	KOH	30	290°	1.10	18.4
8	$C_{10}H_{13}.SO_3Na$	7.64	KOH	7.5	300°	0.91	18.8
9(a)	$(C_{10}H_{13}.SO_3)_2Ca.2H_2O$	10.00	KOH	8.8	300°	3.16	52.9
10(a)	$(C_{10}H_{13}.SO_3)_2Ca.2H_2O$	10.00	KOH	8.8	300°	1.68	28.9
11(a)	$(C_{10}H_{13}.SO_3)_2Ca.2H_2O$	10.00	NaOH	6.4	290°	0.74	12.4

(a) Crucible covered during the fusion.

Other fusions conducted under different conditions gave only small yields of carvacrol and served to show the great difficulty of duplicating results. This is illustrated by Fusions 9 and 10 made under identical conditions.

IDENTIFICATION OF CARVACROL—The carvacrol obtained was identified as follows: 2.5 g. of the phenol were dissolved in dilute KOH and made up to 1.5 liters. Six grams of KNO_2 were then added and after it had dissolved the solution was strongly acidified with sulfuric acid. In a short time the carvacrol nitrite rose to the surface in a flocculent condition. The nitrite crystallized very readily, using hot 50 per cent alcohol, but after several crystallizations the compound was still impure and melted at about 147°.

It was found that the nitrite was insoluble in petroleum ether and this property afforded an easy means of purification. The carvacrol nitrite was dissolved in a minimum amount of chloroform which was slowly dropped, with stirring, into a considerable volume of petroleum ether. The precipitate was finally crystallized from alcohol. The pale yellow needles melted at 153–4°. When heated slowly they melted at 150–152°.

SUMMARY

Sulfite turpentine, consisting largely of cymene, can be used for the production of carvacrol and toluene.

FOREST SERVICE
FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN

THE EFFECT OF INCOMPLETE DISTILLATION ON THE YIELD OF PRODUCTS IN THE DESTRUCTIVE DISTILLATION OF BIRCH

By R. C. PALMER
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OBJECT OF TESTS

In most hardwood distillation plants a certain amount of the wood comes out of the retorts after distillation as "brands" or "bones," that is, pieces incompletely charred. When a plant finds it necessary for economic reasons to use wood that has been insufficiently seasoned or wood excessively wet with rain or snow, it is difficult to complete the distillation in the required 24 hours. Under such conditions the amount of brands is likely to be large, amounting to as much as 8 or 10 per cent of the charge. Usually the brands are redistilled, although they are not considered as new raw material. There is no agreement among operators as to what yields are obtained by distilling the wood in two stages, that is, whether there is actually any gain or loss in products by this procedure. To the knowledge of the author, the literature reveals no data on this point. A few experiments were therefore made to determine just what effect incomplete distillation had on the yield of products in the destructive distillation of hardwood and how yields from stopping the distillation and then redistilling the residue compared with the yields from a single operation.

EXPERIMENTAL PROCEDURE

Yellow birch cord wood reduced to pieces about $2^1/_2$ in. by $2^1/_2$ in. by 16 in., not very well seasoned, was distilled in a semi-commercial laboratory retort holding about 50 lbs. of wood. The temperature in the empty retort was raised to about 340° C. and a specially constructed basket containing the wood was then quickly introduced. The start of the distillation was then similar to the start of a commercial distillation where a new charge is placed in a retort immediately after drawing out the hot charcoal from a run that has just been completed. The distillations were carried on according to the best practice of temperature control, that is, regulating the fire so that the rate of rise of temperature in the retort was decidedly decreased after the tar began to be formed. One run was made in which the distillation was normally carried to completion. In two other runs the fire was turned off when it was obvious from the amount of distillate, temperature, etc., that the distillation was not complete. Different stopping points were selected for the different runs. As the distillation had not reached the point of marked exothermic reaction in these runs it was checked very quickly after the fire was turned off.

After cooling to room temperature the retort was opened and all brands were separated from charcoal. Any stick which was brown in color, or which could not be readily fractured by a moderate blow with a hammer, was considered a brand. All the brands from incomplete distillations were allowed to remain out of doors during a heavy rain until they had absorbed water to about $3^1/_2$ per cent of the dry weight and were then completely distilled as if they were normal wood.