solvents with increasing ketone content is probably the result of greater solvation of the polymers containing a high percentage of electronegative carbonyl groups. There was little variation in water resistance.

In comparing the polymers with GR-S, the range in properties among the four experimental polymers themselves should be borne in mind—for example, the 15% ketone copolymer was slightly superior to GR-S in rebound, while the 45% ketone copolymer was much inferior. However, a few generalizations can be made about the group as a whole. The methyl isopropenyl ketone copolymers were superior to GR-S in laboratory processing characteristics, tensile strength, hot tensile strength, modulus, resistance to hot flex cut growth, and resistance to swelling by iso-octane and hot motor oil, which had a remarkably small effect. The tensile properties of the ketone-butadiene copolymers are outstanding when the brittle points of the compositions and the test temperatures are considered. Borders and Juve (*6*) have shown a relation between the tensile strengths of tread stocks and ΔT, the temperature interval between the brittle point and the test temperature. Their data for hevea rubber tread compounds fall on one curve, showing decreasing tensile with increasing ΔT, while data for a variety of butadiene copolymers fall on another curve which is 1000 to 1600 pounds per square inch lower for a given ΔT. The values the authors have obtained for the ketone-butadiene copolymers (particularly 25 and 35% ketone) when plotted in this manner are equivalent to those for natural rubber tread compounds. This improved performance may arise from either or both of two causes: (1) a more nearly linear polymer (which is suggested by the soluble, high-Mooney-viscosity polymers that can be prepared, *11*) and (2) some specific interaction which takes place between the $—COCH_3$ in the polymer chains and the carbon black, although interaction among $—COCH_3$ groups is not great enough to raise the brittle point unduly.

The methyl isopropenyl ketone copolymers were somewhat inferior in elongation, rebound, heat build-up, and resistance to swelling by benzene, butyl acetate, and ethylene dichloride. Tear strength, hardness, compression set, cold embrittlement, and resistance to swelling by water were about the same as for GR-S.

The effect of per cent of ketone on aging seemed somewhat variable. The effect of aging on modulus and elongation was somewhat less than for GR-S, but tensile strength of the ketone copolymer was affected somewhat more. The notable superiority of the ketone copolymers to GR-S in resistance to hot flex cut growth held for both unaged and aged (96 hours at 212° F., 100° C.) samples with the exception of 15% ketone copolymers. This superiority in hot flex cut growth is especially noteworthy when the high modulus is taken into consideration.

LITERATURE CITED

(1) Am. Soc. Testing Materials, D 395–40T (Method B).
(2) *Ibid.*, D 430–40.
(3) *Ibid.*, D 623–41T.
(4) *Ibid.*, D 471–43T.
(5) *Ibid.*, D 746–44I.
(6) Borders, A. M., and Juve, R. D., Ind. Eng. Chem., 38, 1066 (1946).
(7) Dreisbach, R. R. (to Dow Chemical Co.), U. S. Patent 2,383,782 (Aug. 28, 1945).
(8) *Ibid.*, 2,386,448 (Oct. 9, 1945).
(9) *Ibid.*, 2,394,756 (Feb. 12, 1946).
(10) *Ibid.*, 2,385,695 (Sept. 25, 1945).
(11) Gould, C. W., and Hulse, G. E., Ind. Eng. Chem, 41, 1045 (1949).
(12) Meisenburg, K. (to I. G. Farbenindustrie, A.-G.), U. S. Patent 1,901,354 (March 14, 1933).
(13) Morgan, G., Megson, N. J. L., and Pepper, K. W., *Chemistry and Industry*, 16, 885 (1938).

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1-Trichloro-2,2-bis(*p*-methoxyphenyl)ethane (Methoxychlor)

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Methoxychlor, the methoxy analog of DDT, is prepared by the condensation of anisole with chloral in the presence of sulfuric acid by a procedure analogous to that used for DDT itself. However, commercial concentrated sulfuric acid is used instead of 100% acid or oleum because the reactivity of anisole as compared to chlorobenzene makes the use of strong acid neither necessary nor advisable. The effect of several variables upon the yield and quality of product is described and a pilot plant procedure is proposed.

THE methoxy analog of DDT, also called methoxychlor (*1*), was first prepared in 1893 by Elbs (*5*) by the condensation of chloral hydrate with anisole in the presence of concentrated sulfuric acid, glacial acetic acid being used as a diluent. Harris and Frankforter (*9*) prepared the compound in 1926, using anhydrous aluminum chloride as the condensing agent at 0° C. in the presence of a tenfold volume of carbon disulfide.

The Geigy group of workers (*10*) reported in 1944 that this compound possessed effectiveness as an insecticide, but presented no details as to the species of insects upon which it had been tested, nor as to the concentrations required for toxicity. Martin and Wain (*11*) and Siegler and Gertler (*13*) also reported the compound to have some insecticidal activity. Prill and his coworkers (*12*) reported the results of tests on houseflies which indicated that the compound might have value in special cases as an adjunct or alternate to DDT itself. Others have studied the toxicity of the compound for insects (*2, 14*).

This study was undertaken in order to determine the optimum conditions for the sulfuric acid condensation of chloral with anisole.

DIMORPHISM

The values for the melting point of this compound which have been reported by the workers named above and others are in disagreement. Elbs (*5*) reported a melting point of 92° C. Fritsch and Feldman (*8*) prepared the compound by essentially the same procedure as Elbs, and stated that the correct value of the melting point was 89° C. Frankforter and Kritchevsky

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TABLE I. SUMMARY OF TRIAL PREPARATIONS OF METHOXY ANALOG[a]

Expt.	Excess Chloral, %	Acid, Ml.	Temp., °C. ± 2	Time of Acid Addn., Min.	Extra Stirring Time, Min.	Wash Treatment[b]	Yield, %	Setting Point, ° C.
A	0	500	32	..	30	1 l., 60° C. 200 ml. alc.	90.5	62
B	0	290	50	27	30	1.5 l., 55° C. 500 ml. alc.	84.5	65.5
C	5	305	50	30	..	2.5 l., 50° C. 2.5 l.	85.5	57
D	10	305	57	30	Stand overnight	2.5 l., 50° C. 2.5 l., 40° C. 400 ml. alc.	83.6	53
E	0	265	60	20	120	2.5 l. 2.5 l., 50° C.	86.6	51
F	2	265	36	85	..	3 l., 50° C. 3 l. 2.5 l.	92.6	64
G	5	245	32	100	..	4 l. 4 l., overnight 2 l.	92.0	67
H	5	245	35	120	..	3 l., 12 hr. 3 l., 24 hr.	82.4	68
I	5	245	37	[c]	..		81.4	68
J	5	245	37	..	..	2 l. 4 l.	83.8	61
K	5	Approx. 125	37	..	..		58.4	81.5
L	5	245	37	..	..	[d]	57.1	83
M	10	220	37 50	..	..		91.1	67
N	5	245	30	..	..	[e]	90.2	70.5
O	2	245	30	..	..	[f]	94.4	70

[a] 500 g. of anisole were used in each case.

[b] The figures given represent the volumes of successive washes with water at room temperature or the temperature indicated; in E and succeeding experiments, the product was neutralized by the addition of an excess of sodium carbonate to one of the washes.

[c] In this and succeeding experiments, the acid was added as rapidly as was possible while maintaining the desired temperature, using city water as the external cooling medium; this factor may be considered practically constant.

[d] 1000 ml. glacial acetic acid added; product washed with ethanol.

[e] 1200 ml. ethylene dichloride added as thinning agent.

[f] 350 ml. carbon tetrachloride added as thinning agent.

(7) prepared the compound by the condensation of chloral with anisole through the agency of anhydrous aluminum chloride, and found its melting point to be 78° C. Concerned with the discrepancy in melting point between their product and that of Elbs, they repeated the preparation according to the latter's procedure, and obtained a product identical in melting point with their first product—namely, 78° C. They proposed no explanation for the disagreement. Later Harris and Frankforter (9) prepared a number of alkyl ether analogs by a modification of Frankforter's earlier procedure (7). Their report gave 94° C. as the melting point of the methoxy analog, and made no mention of the discrepancy between that value and the 78° C. value previously published by the senior author. In both publications a value of 109° C. was reported by Frankforter as the melting point of the ethylene derivative resulting from the dehydrochlorination of the compound. Fritsch and Feldman (8) reported a value of 113° C. for the ethylene derivative and Elbs (5) apparently did not prepare this compound. Recently Prill, Hartzell, and Arthur (12) prepared the methoxy analog and obtained a melting point of 89° C. Cristol (4) gave the melting point of this compound as 87° to 88° C. (corrected).

In the first preparation of the methoxy analog by Schneller and Smith the procedure of Elbs was followed strictly, and the melting point of the product was 78.0° to 78.2° C. (corrected) after five recrystallizations from 95% ethanol. Two subsequent preparations gave products which, after a single crystallization from 95% ethanol, melted at 74° to 75° and 70° to 71° C. (uncorrected), respectively. Analysis of the sample melting at 78.0° to 78.2° C. gave a value of 30.85% chlorine (theoretical, 30.77%). The material was subjected to dehydrochlorination and the resulting product melted at 108.5° to 109° C. (corrected).

However, in subsequent experiments on a larger scale (Table I) a material was obtained which after two recrystallizations from ethanol had a melting point of 86.5° to 87.5° C. (uncorrected) and upon dehydrochlorination gave an ethylene derivative with a melting point of 108.5° to 109° C. (corrected). Thereafter the preparation of the lower melting material could not be repeated.

The following observations indicated that dimorphism was involved:

When the material which melted at 78.0° to 78.2° C. in a capillary tube was allowed to congeal, a redetermination of its melting point gave a value of 86° to 88° C. The transformation involved no change in weight. Solutions of the lower melting material when allowed to crystallize invariably gave a product with the higher melting point. Solutions in ethanol of both types of crystals had the same ultraviolet absorption spectrum.

The transformation from the lower melting form to the higher could not be reversed. The attempts to accomplish this reversal included pouring a solution of the high melting material into an aqueous suspension of the finely divided low melting material, seeding an almost saturated solution of the high melting material at 70° C. with the low melting material, and seeding the fused but supercooled high melting material at 70° C. with the low melting material.

PREPARATION OF THE METHOXY ANALOG

The development of a pilot plant procedure involved the trial of various modifications of the procedure of Elbs (5) and of Fritsch and Feldman (8), which consists basically of the gradual addition of sulfuric acid to a mixture of chloral and anisole. The principal variables which affected the yield and the quality of the product were the temperature, the concentration and the quantity of the acid, the rate of the addition of the acid, the relative quantities of chloral and anisole, and the treatment of the product after the completion of the condensation proper. The influence of these variables is discussed in the following paragraphs and is indicated in Table I wherein are summarized the reaction conditions and results of the various experiments.

Fritsch and Feldman (8), using glacial acetic as a diluent, and a reaction temperature of 50° C., obtained a rather pasty product which they found necessary to knead in a mortar with water and then with alcohol in order to purify it. Elbs (5) did not state his procedure for purification, but since his reaction procedure corresponded closely to that of the other workers, his product must have been similar to theirs. In preliminary experiments following the procedure of Fritsch and Feldman, the product was kneaded in a mortar in order to effect preliminary purification. The principal effort, therefore, was expended in attempting to devise a means of obtaining a granular product which could easily be separated, washed, and dried, preferably without the use of alcohol or another solvent as a wash for the solid product, and which would exhibit a setting point within 20° of the melting point of the pure material, in accordance with the commercial practice in the case of DDT (6).

At first (experiments A to F) warm wash water was used to soften the product sufficiently to permit efficient stirring, so as to remove the sulfuric acid and the water-soluble reaction byproducts. Later (experiment G) it was found that a lower reaction temperature combined with a slow rate of acid addition could actually effect the crystallization of the product while it was still in the reaction mixture. In experiment G, shortly after the last portion of the acid had been added, the whole reaction mass turned into a crystalline cake of material which had to be broken up with a hard implement in order to be removed from the vessel. In the next experiment (H) the reaction was carefully watched as the final portions of the acid were added, and when the crystallization—which was rapid when once it had started—had proceeded to such an extent that the slurry could barely be poured from the reaction vessel, the slurry was poured into a large quantity of water. By this expedient the formation of a solid or lumpy mass was avoided and effective washing with cold water was made possible. However, the fact that the reaction had been terminated prematurely was evidenced by the low yield, 82.4%, and by a certain greasiness of the crystalline product—owing to unreacted anisole—which would have necessitated washing with alcohol.

Therefore, the problem was to permit the reaction to proceed as far as possible toward completion and yet to prevent the solidification of the reaction mass with the resulting danger to the equipment and the difficulty of handling a caked product.

In experiment K, the accidental entry of water into the reaction vessel necessitated a termination of the reaction when only half of the expected quantity of acid had been added. The product had a setting point of 81.5° C. but the yield was very low.

In experiment L, the crystallization of the reaction slurry had already begun when four fifths of the acid had been added. Glacial acetic acid was then added and the final one fifth of sulfuric acid was added gradually over an interval of 45 minutes. The final product was greasy owing to unreacted anisole, and required washing with alcohol. The yield of product with a setting point of 83° C. was 57.1%. The addition of glacial acetic acid had practically stopped the reaction, and, therefore, had defeated the purpose for which it had been intended.

Meanwhile, it had been reported (*3*) that in the case of DDT, considerable advantage resulted from the following purification procedure: dissolving the reaction product in ethylene dichloride, washing the solution with water and then with an alkaline solution, steam distilling the ethylene dichloride, and finally pouring the molten product out on a large surface to solidify. Such a procedure would coincide with the use of such a solvent for the additional purpose of thinning the reaction mass. Accordingly, ethylene dichloride and also carbon tetrachloride were used in experiments N and O, respectively. In each case the addition of the solvent was begun at the point where the incipient crystallization of the reaction product had increased the viscosity considerably. The gradual addition of the solvent maintained the viscosity at a sufficiently low level to permit the reaction to approach completion with the continued addition of the final portions of the sulfuric acid. Of the two solvents, the use of carbon tetrachloride resulted in a considerably higher yield, despite the much lower proportion of excess starting chloral, and also offered the advantage of a more rapid separation of the product-solvent slurry from the supernatant wash liquors as a result of the higher density.

The foregoing observations and considerations were used as the basis for a pilot plant procedure for the manufacture of the methoxy analog. The method was proposed for use in an already existing installation which comprised, in principal part, a 300-gallon jacketed enamel-lined enclosed reactor with an anchor-type stirrer and equipped for distillation. The following procedure gave in an initial run a yield of 88.1% and the product had a setting point of 69° C.

METHOD FOR PILOT PLANT PRODUCTION OF METHOXY ANALOG

STARTING MATERIALS. The quantities specified (Table II) are for a batch of 1400 pounds of the finished analog and are based on an over-all yield of 90%. The batch size was calculated on the basis of 300-gallon working capacity of the reactor used in the condensation.

PROCEDURE. The anisole and the chloral are mixed and the acid is added slowly with vigorous agitation. The temperature is maintained at 25° to 30° C. by means of external cooling. Higher temperatures reduce the yield and lower the purity of the product. With good agitation, and a cooling water temperature of 15° C., the reaction time is less than 1 hour.

TABLE II

Materials	Lb.
Chloral (including 2% excess[a]) "DDT grade"	877
Anisole, redistilled	974
Sulfuric acid (57.3 gal.) 66° Baumé	875
Carbon tetrachloride (83.0 gal.)	1100
Sodium carbonate	120

[a] Chloral was originally used in excess in preference to anisole because of the relative ease of its removal from the condensation product by washing with water. However, in view of the use of carbon tetrachloride in connection with the washing, it would appear more desirable to use anisole as the excess component. The excess anisole would be steam distilled together with the carbon tetrachloride, and could be used directly in that solvent in the next batch.

As the reaction approaches completion, the reaction mass tends to thicken excessively as a result of the incipient crystallization of the reaction product. At this point, the carbon tetrachloride is added in sufficient quantities to keep the mixture fluid enough to permit the continuation of the stirring. The stirring is continued for 1 hour after the first addition of carbon tetrachloride.

The reaction mixture is quenched by blowing or pumping it out of the reactor into a tank containing 700 gallons of cold water and stirring well. The temperature of the resulting mixture is 45° to 50° C. The supernatant aqueous acid layer is separated by suitable means and discarded.

The separated slurry is washed by stirring with hot water, allowing to separate, and decanting the water layer. This treatment is repeated, and this time sodium carbonate is added to the stirred mixture in sufficient quantity to effect neutralization. The washed slurry is run back into the reactor, which is to serve also as a still.

The carbon tetrachloride is distilled with steam and the molten methoxy analog is run out of the still into suitable containers for solidification. The solidified product is ready for use as the technical grade material.

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LITERATURE CITED

(1) Anon., *Chem. Eng. News*, **26**, 476 (1948).
(2) Barnes, S., *Bull. Entomol. Research*, **36**, 273 (1945).
(3) Coster, L. R., personal communication.
(4) Cristol, S. J., *J. Am. Chem. Soc.*, **67**, 1498 (1945).
(5) Elbs, K., *J. prakt. Chem.*, 47, [2] 68 (1893).
(6) Fleck, E. E., and Preston, R. K., *Soap Sanit. Chemicals*, **21**, No. 5, 111 (1945).
(7) Frankforter, G. B., and Kritchevsky, W., *J. Am. Chem. Soc.*, **36**, 1511 (1914); **37**, 385 (1915).
(8) Fritsch, P., and Feldman, F., *Annalen*, **306**, 77 (1899).
(9) Harris, E. E., and Frankforter, G. B., *J. Am. Chem. Soc.*, **48**, 3144 (1926).
(10) Läuger, P., Martin, H., and Müller, P., *Helv. Chim. Acta*, **27**, 892 (1944); English translation published in New York by Geigy Co., Inc., 1945.
(11) Martin, H., and Wain, R. L., *Nature*, **154**, 512 (1944).
(12) Prill, E. A., Hartzell, A., and Arthur, J. M., *Science*, **101**, 464 (1945).
(13) Siegler, E. H., and Gertler, S. I., *J. Econ. Entomol.*, **37**, 845 (1944).
(14) Sleesman, J. P., and Wilson, J. D., *Vegetable Growers Assoc. Am., Ann. Rept.*, **1945**, 182.

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