hydroxide (in which it was soluble) V yielded 43% of its chlorine after one hour of boiling. The same treatment of chloromethanesulfonic acid IV changed only 20% of the chlorine to chloride ion, qualitatively suggesting that the decomposition of V had also taken place by carbon–sulfur fission rather than by preliminary amide hydrolysis. One may even conjecture, without evident means for proof, that the 20% decomposition of chloromethanesulfonic acid, IV, in alcoholic sodium hydroxide solution may also be an example of carbon–sulfur fission.

Experimental Part

The physical properties of chloromethanesulfonyl chloride and its derivatives previously reported do not agree with those determined by the authors.

Chloromethanesulfonyl Chloride, I.—Prepared by the action of chlorine on a cold water suspension of trithiane: b. p. 77° (23 mm.), n^{20}D 1.4868, n^{25}D 1.4851, $d^{0^\circ}_4$ 1.6971, $d^{20^\circ}_4$ 1.6672, $d^{30^\circ}_4$ 1.6530 (*cf.* Kostsova,[3] Lee and Dougherty[4]).

In fractionating 150 g. of I through an efficient glass spiral-filled column a small amount of colorless solid collected in the condenser at the start of the distillation but was dissolved by the succeeding liquid. The first fraction containing most of the dissolved solid had an index of refraction n^{20}D 1.4945. In succeeding fractions the index of refraction reached a minimum at n^{20}D 1.4868. In preparations when the chlorination was incomplete a yellow product was obtained. The product from one such preparation was distilled from an ordinary Claisen flask into four fractions as follows[8]

Fraction	A	B	C	D
n^{24}D	1.5021	1.4977	1.4945	1.5175

Chloromethanesulfonamide, II.—Colorless prisms from mixed ether–petroleum ether; needles from benzene; very soluble in water; m. p. 73–74°, b. p. 185° (20 mm.) (*cf.* Kostsova).[3] *Anal.* Calcd. for CH_4O_2NClS: N, 10.81. Found: N, 10.68.

Chloromethanesulfonanilide, III.—Colorless polygonal prisms from 50% alcohol, m. p. 81–82°. *Anal.* Calcd. for $C_7H_8O_2NClS$: N, 6.81. Found: N, 6.89.

Chloromethanesulfon-*p*-Toluide, $ClCH_2SO_2NHC_6H_4$-CH_3-*p*.—Glass-like prisms from ether–petroleum ether, m. p. 96–97°. *Anal.* Calcd. for $C_8H_{10}O_2NClS$: N, 6.38. Found: N, 6.31.

Chloromethanesulfondiethylamide, V.—Colorless plates from ether, insoluble in water, m. p. 45°. *Anal.* Calcd. for $C_5H_{12}O_2NClS$: N, 7.57. Found: N, 7.62.

Summary

1. The properties of chloromethanesulfonyl chloride and several of its derivatives are described.

2. The chlorine of the chloromethanesulfonamides is not readily removed in metathetical reactions and these compounds are not promising intermediates for the preparation of aminomethanesulfonamides.

3. The chloromethanesulfonamides are decomposed by sodium hydroxide by fission of the molecule between the carbon and sulfur atoms rather than by preliminary amide hydrolysis.

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[8] These results suggest that the chlorination of trithiane produces at least two substances in addition to I. It is the intention of the junior author to investigate further the identity of these other products to determine, if possible, the mechanism of the chlorination reaction.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Anthocyanidin-Like Pigments from α-Naphthohydroquinones

BY MARY FIESER AND LOUIS F. FIESER

In an investigation of the condensation of β-naphthohydroquinone with aldehydes under the influence of hydrogen chloride in benzene solution, it was found that two molecules of the former compound react with one of the aldehyde to give colorless substances of the type $C_{10}H_6(OH)$-$OCHArC_{10}H_5(OH)_2$.[1] The sensitive substances are cleaved easily by concentrated sulfuric acid, for example to the enolic tautomer of 4-benzyl-1,2-naphthoquinone. α-Naphthohydroquinone was observed to react with aldehydes in an apparently similar manner, but no crystalline products could be isolated. The course of the reaction evidently is highly dependent upon the conditions, for on using a mixture of acetic and hydrochloric acids in place of dry hydrogen chloride and benzene we obtained pigments of the type first described in a preliminary report by Wurgaft,[2] who stated that in acetic acid solution α-naphthohydroquinone condenses with benzaldehyde in the presence of hydrogen chloride to give a sparingly soluble, crystalline red compound of the formula ArC_{21}-

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[1] Fieser and Fieser, THIS JOURNAL, **61**, 596 (1939).

[2] Wurgaft, *J. prakt. Chem.*, **49**, 551 (1894).

$H_{14}O_4Cl \cdot H_2O$. He observed that the pigment dissolves in alkali with a beautiful, deep blue color which fades on standing, and he reported, albeit without adequate analytical characterization, the formation of a chlorine-free base, an acetate, and a leuco acetate. Raudnitz and Puluj[3] encountered a similar pigment on attempting to condense isovaleraldehyde with α-naphthoquinone in the manner of the Hooker[4] iso-β-lapachol synthesis. They found that other aldehydes condense similarly and that the same pigments are produced in much better yield if α-naphthohydroquinone is employed in place of the quinone. Raudnitz and Puluj analyzed the pigments from seven aldehydes and concluded that they all can be represented by a formula differing from that of Wurgaft by the absence of a molecule of water of hydration. They considered the reaction to be $2C_{10}H_6(OH)_2 + ArCHO + HCl + [O] \rightarrow ArC_{21}H_{14}O_4Cl + 2H_2O$.

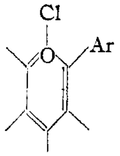
One of the recrystallized products studied in the present work when dried in vacuum at a moderate temperature was found to have a composition corresponding to Wurgaft's formulation, while another corresponded to the results of Raudnitz and Puluj. Samples dried in vacuum at 150° lost further weight and were hygroscopic; in one case the loss was approximately that calculated for the elimination of a further molecule of water. Drying at 200° resulted in decomposition. Analyses of the pigments as such are thus rather inconclusive. Since the chlorine atom seemed to be present in salt linkage, it seemed possible that the pigments might form other salts more suitable for analytical characterization. It was found that a picrate can be prepared by adding picric acid to a blue solution of the pigment in alcoholic–aqueous sodium carbonate. The picrates are practically insoluble in all solvents tried except boiling nitrobenzene. By rapid crystallization from this solvent, satisfactory samples were obtained of the products derived from benzaldehyde and *m*-tolualdehyde. These are not hygroscopic and the analyses of both salts indicate the formula $ArC_{21}H_{12}O_3 \cdot C_6H_2O_7N_3$. This indicates that the chlorides analyzed by Raudnitz and Puluj were monohydrates of pigments of the formula $ArC_{21}H_{12}O_3Cl$, and that Wurgaft's compound was a dihydrate.

We were unable to isolate chlorine-free bases in a crystalline condition, but found that by acetylation of the pigments in pyridine solution colorless acetates can be prepared of the empirical formula $ArC_{21}H_{11}O_2(OCOCH_3)_2$. This suggests that the pigment contains two phenolic groups and that the halogen is present in oxonium salt linkage, hydrolysis giving rise to a tertiary carbinol or pseudo base, $ArC_{21}H_{10}O(OH)_2Cl \rightarrow ArC_{21}H_{10}O(OH)_2OH$. The third oxygen atom must be present in oxidic linkage.

The pigments are reduced readily in alkaline solution by sodium hydrosulfite and the blue color is restored by air oxidation. Reductive acetylation, using acetic anhydride and sodium acetate, gave colorless, halogen-free products of the formula $ArC_{21}H_{11}O(OCOCH_3)_2$. The parent reduction product therefore is a leuco base, $ArC_{21}H_{11}O(OH)_2$, and differs from the pseudo base in having hydrogen in place of the tertiary hydroxyl group.

The relationship of the pigments to the two types of derivatives corresponds to that existing in the anthocyanidin series, and indeed the pigments show the properties characteristic of the anthocyanidins. In the form of the oxonium chlorides, the latter substances retain water of crystallization tenaciously; they undergo reversible reduction, and they dissolve in alkali to give deep blue solutions which fade as the result of hydrolysis to the pseudo base form.

One possible formulation would involve the intermediate formation of an ether similar to that isolated in the β-naphthohydroquinone series, with ultimate formation of a pigment having the grouping I. The pseudo base, however, would have a ketol grouping (II) which would be expected to suffer fission under the influence of pyridine. A more plausible interpretation is that the aldehyde condenses symmetrically with two molecules of α-naphthohydroquinone in the ortho position, as in the condensation of benzaldehyde with β-naphthol,[1] with subsequent oxidation to the pigment III. The pseudo base would then have the more stable structure IV. Degradation experiments thus far have been unsuccessful.



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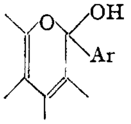

II

A red pigment closely resembling those described was encountered as a by-product in the

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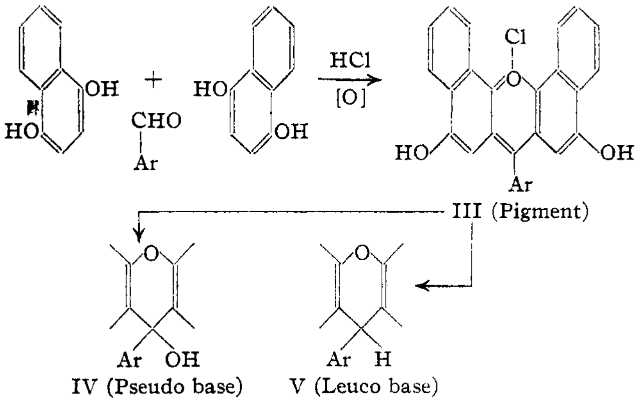
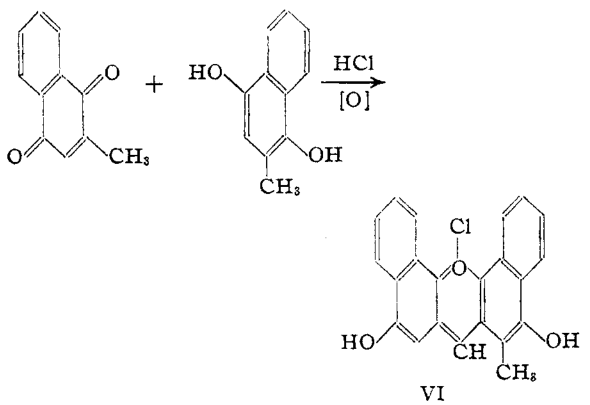
[3] Raudnitz and Puluj, *Ber.*, **64**, 2212 (1931).

[4] Hooker, *J. Chem. Soc.*, **69**, 1355 (1896).



course of work on the synthesis of vitamin K$_1$. When either 2-methyl-1,4-naphthoquinone or its hydroquinone was heated with phytol or similar component in the presence of a mineral acid, or even oxalic acid, a deep red, sparingly soluble pigment was formed in varying amounts. Further study has shown that the pigment is obtainable from the naphthalene derivative and a mineral acid alone. The best yield (40–44% by weight) is obtained when a mixture of equal parts of the quinone and hydroquinone is employed. The pigment contains halogen and dissolves in alkali with a deep blue color which fades on standing. It does not dissolve to an appreciable extent in any of the usual organic solvents, but, since it can be caused to separate from the reaction mixture in a microcrystalline form, samples prepared from filtered solutions were washed extensively and submitted to analysis. The compound retains water very tenaciously and the dried substance is hygroscopic. Extensive drying at 150° gave material of constant weight and the analyses of the anhydrous substance indicate the formula $C_{22}H_{15}O_3Cl$. 2,6-Dimethyl-1,4-naphthoquinone afforded an analogous pigment of the composition $C_{22}H_{13}(CH_3)_2O_3Cl$.



VI

Attempts to characterize the pigments further were unsuccessful; the sparing solubility of the substances imposes a serious limitation on the scope of experimentation. The pigments obviously exhibit anthocyanidin-like properties, and they resemble the colored products of the aldehyde condensation reaction sufficiently closely to suggest that they are similarly constituted. A possible formulation of the pigment from methylnaphthoquinone and methylnaphthohydroquinone is shown in formula VI.

Experimental Part[5]

Pigments from α-Naphthohydroquinone and Aldehydes

Characterization of the Pigments.—The substances were prepared from α-naphthohydroquinone according to the directions of Raudnitz and Puluj,[3] the yield of once recrystallized (glacial acetic acid) material being 70–75%. We likewise found that the yield was much lower when the quinone was employed. Thus the condensation of 1 g. of α-naphthoquinone with benzaldehyde afforded 0.7 g. of non-lustrous crude material which yielded only 0.3 g. of satisfactory pigment on recrystallization. A similar condensation with 1 g. of α-naphthohydroquinone gave 0.80 g. of crystalline pigment having the bronze luster characteristic of the pure material; a mixture of 0.5 g. of α-naphthoquinone and 0.5 g. of α-naphthohydroquinone afforded 0.85 g. of pure pigment.

The **pigment from *m*-tolualdehyde** was prepared by adding 12 cc. of concentrated hydrochloric acid to a solution of 5.6 g. of α-naphthohydroquinone and 4 cc. of the aldehyde in 60 cc. of glacial acetic acid and heating the solution on the steam-bath. Dark red crystals began to separate after fifteen minutes, and after forty-five minutes the mixture was cooled and the product collected; yield 5.5 g. Repeated recrystallization from acetic acid (sparingly soluble) was attended with little loss of material or alteration in the appearance of the dark red microcrystals having a bronze luster. The sample was dried in vacuum at 80°.

Anal. Calcd. for $C_{28}H_{19}O_3Cl \cdot 2H_2O$: C, 70.81; H, 4.88. Found: C, 70.75, 70.87; H, 4.65, 4.69.

The recrystallized product from ***n*-butyraldehyde**[3] was dried in a xylene boiler at the vacuum of the water pump and analyzed with the following results.

Anal. Calcd. for $C_{24}H_{19}O_3Cl \cdot H_2O$: C, 70.48; H, 5.18. Found: C, 70.63; H, 5.61.

Some of the same sample was heated for one hour further at 105° at 1–2 mm. pressure and no loss in weight was observed. When it was then heated in vacuum for four hours at 145°, the loss in weight amounted to 2.83%, as compared with the value 4.40% calculated for the complete dehydration of a monohydrate.

The pigment from **benzaldehyde**[2,3] after being dried at 80° was found to lose 3.46% weight when dried for a prolonged period at 150°. This corresponds approximately with the value 3.91% calculated for conversion of the di-

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[5] Microanalyses by Lyon Southworth and H. S. Wight.

hydrate to the monohydrate, and the analysis of the dried sample is close to that calculated for the monohydrate.

Anal. Calcd. for $C_{27}H_{17}O_3Cl{\cdot}H_2O$: C, 73.30; H, 4.29. Found: C, 73.89; H, 4.63.

When the sample was then dried at 200° it suffered decomposition.

The substance dissolves partially in dilute sodium carbonate solution in the cold with a deep purple-blue color, and on application of heat the blue is rapidly discharged and powdery red material is precipitated. The pigment dissolves readily in cold dilute alkali to give an indigo blue solution; on standing for two or three minutes (or on heating) this changes to purple, and in about one-half hour the solution becomes deep brownish-red and some dull red material precipitates. The addition of hydrochloric acid then causes the separation of a flocculent red precipitate. When collected and crystallized, this material gives the tests of the original pigment. When sodium hydrosulfite is added to a freshly prepared, deep blue solution of the pigment in alkali the color is at once discharged and a colorless or yellowish vat results. On shaking this with air the blue color reappears. If the vat is acidified with acetic acid a flocculent red product is precipitated; after coagulation by boiling and crystallization from acetic acid, material corresponding to the original pigment is obtained. The pigment partly dissolves in cold pyridine with a cherry red color, and on heating the solution on the steam-bath the color fades to a pale pink. Water then precipitates an oily, pale yellowish product, and if this is treated with hydrochloric acid the color of the pigment is restored. Extraction of the oil with ether afforded only a dark resin.

Picrates.—The procedure found satisfactory for the preparation of these derivatives consisted in adding a saturated solution of picric acid in alcohol to a freshly prepared, deep blue solution of the pigment in a mixture of dilute aqueous sodium carbonate and alcohol. The picrate separates at once, in the form of deep red microcrystals having a bronze sheen. The product from *n*-butyraldehyde proved to be particularly sensitive to boiling nitrobenzene, and attempts to crystallize it were unsuccessful. The picrates of the pigments containing aryl radicals are more stable and could be crystallized by adding boiling nitrobenzene to the solid material, filtering rapidly, and cooling the solution at once. The picrate of the **benzaldehyde pigment** separated in well-formed, lustrous bronze plates, which when ground gave a red powder. It decomposes above 300° without melting.

Anal. Calcd. for $C_{27}H_{17}O_3{\cdot}C_6H_2O_7N_3$: C, 64.17; H, 3.10. Found: C, 64.47; H, 3.04.

The picrate of the ***m*-tolualdehyde series** crystallized from nitrobenzene in dark red microcrystals having a metallic reflex.

Anal. Calcd. for $C_{28}H_{19}O_3{\cdot}C_6H_2O_7N_3$: C, 64.65; H, 3.25. Found: C, 65.04; H, 3.50.

Diacetates of the Pseudo Bases.—The best results were obtained by suspending 0.5 g. of the pigment in 4 cc. of pyridine, adding 1 cc. of acetic anhydride, and allowing the mixture to stand at room temperature with occasional stirring. The pigment dissolved in about two hours, and after standing overnight the color had faded to pale pink. On pouring the solution into water a pale yellow solid separated which appeared to be hydrated, for when the mixture was heated to boiling the product first became oily and then changed to a granular solid. The best solvent medium found for crystallizing the diacetates is a mixture of ethyl acetate and ligroin. Although the substances show no signs of decomposition in this mixture, the solutions tend to remain supersaturated and afford only microcrystalline material, and the recovery is low. The yield of once crystallized material was 0.2–0.25 g. When warmed with glacial acetic acid the diacetates turn yellow and then dissolve to give an orange-red solution.

The diacetate from the **benzaldehyde pigment** formed colorless, granular microcrystals which darken at 240° and decompose at 265–270° (Wurgaft,[2] 246°).

Anal. Calcd. for $C_{31}H_{22}O_6$: C, 75.90; H, 4.52. Found: C, 75.63; H, 4.61.

The diacetate of the ***n*-butyraldehyde series** separated slowly from ethyl acetate–ligroin as a mass of fine, faintly yellow, cottony needles; it darkens at about 240° and decomposes in the range 265–275°.

Anal. Calcd. for $C_{28}H_{24}O_6$: C, 73.66; H, 5.30. Found: C, 73.38; H, 5.14.

Diacetates of the Leuco Bases.—For reductive acetylation the pigment was heated with acetic anhydride and zinc dust at the boiling point until the red color had faded, and sodium acetate was then added and the mixture boiled for ten minutes longer. The hot solution was filtered and the product precipitated by dilution with water. The derivative from **benzaldehyde** crystallized from benzene–ligroin in the form of small white, glistening plates. The substance began to darken at 230° and decomposed at about 260–270°.

Anal. Calcd. for $C_{31}H_{22}O_5$: C, 78.46; H, 4.68. Found: C, 78.10; H, 4.81.

The ***n*-butyraldehyde derivative** crystallized from alcohol in pale yellow needles, which decomposed at 275–280°.

Anal. Calcd. for $C_{28}H_{24}O_5$: C, 76.34; H, 5.49. Found: C, 76.01; H, 5.13.

Pigments from 2-Methyl- and 2,6-Dimethyl-1,4-naphthohydroquinone

The pigments were prepared satisfactorily by adding 1 cc. of concentrated hydrochloric acid to a solution of 0.5 g. of the quinone and 0.5 g. of the hydroquinone in 10 cc. of glacial acetic acid and heating the solution on the steam-bath. The solution soon became dark red and a microcrystalline product separated. The yield of either pigment collected after one-half hour was 0.40 g., and the amount was about the same (0.44 g.) after a one-hour period of heating. The yield was essentially the same when the hydroquinone alone was employed. When only the quinone was used, the solution turned red and a solid product separated, but this was of poor appearance and on microscopic examination was found to be non-crystalline.

The pigments give no appreciable coloration in boiling alcohol, benzene, ethyl acetate, or nitrobenzene, and are decomposed by boiling with quinoline. They dissolve slowly in cold aqueous alkali to give rich blue solutions; the color fades slowly on standing and rapidly on heating and a reddish-brown solid then separates. The blue color is discharged by the addition of sodium hydrosulfite;

the weakly yellow vat remains unchanged when shaken with air but acquires a pink color on acidification with acetic acid. The pigment dissolves in alcoholic alkali with a bluish-green color which fades rapidly to a dull red-brown.

The samples analyzed were prepared by mixing filtered solutions of the components and washing the collected product thoroughly with alcohol, water, alcohol, benzene, and glacial acetic acid. The pigments were unmelted at 280°. Analyses of samples dried at 80–105° indicated the presence of approximately one molecule of bound water. The results reported were obtained after drying to constant weight at 150° and 1–2 mm. pressure (several hours).

The pigment from **2-methyl-1,4-naphthohydroquinone** formed dark red microscopic needles having a metallic, golden shimmer.

Anal. Calcd. for $C_{22}H_{15}O_3Cl$: C, 72.82; H, 4.16; Cl, 9.78. Found: C, 72.97; H, 4.28; Cl, 9.48.

The product from **2,6-dimethyl-1,4-naphthohydroquinone** was of similar appearance.

Anal. Calcd. for $C_{24}H_{19}O_3Cl$: C, 73.75; H, 4.90. Found: C, 73.77; H, 4.91.

Summary

The pigments obtainable as described in the literature by condensing α-naphthohydroquinone with various aldehydes in acetic–hydrochloric acid solution are assigned the revised formula $Ar(R)C_{21}H_{12}O_3Cl$, largely on the basis of the isolation of anhydrous picric acid salts. The composition and properties, together with the preparation of pseudo base diacetates and leuco base diacetates, suggest that the pigments are oxonium salts of the anthocyanidin type. A formulation is suggested.

Pigments exhibiting analogous properties are produced by the action of hydrochloric and acetic acids on 2-methyl and 2,6-dimethyl-1,4-naphthohydroquinone. These also appear to be oxonium salts of the anthocyanidin type.

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[CONTRIBUTION FROM WALKER LABORATORY, RENSSELAER POLYTECHNIC INSTITUTE]

The Effect of Ultraviolet Light on Methyl Cellulose in Solution

BY L. SPITZE, A. MOORADIAN, R. H. HARTIGAN AND L. A. HANSEN

Although numerous papers have appeared on the action of ultraviolet light on cellulose and its nitric and acetic esters, such work on the ethers of cellulose is less abundant. In a spectrographic investigation of cellulose and cellulose acetate, Rassow and Aehnelt[1] concluded that cellulose absorbs light strongly; varying the viscosity of the solution of an ester does not affect light absorption, but a change in the number of ester groups does affect it considerably. Rassow and Weber[2] report that depolymerization, low viscosity and low light absorption go together. Clement, Riviere and Beck[3] investigated the effect of ultraviolet light on a number of cellulose derivatives and observed that, with cellulose and hydrocellulose, the action is one of polymerizing. The potassium hydroxide index decreases under the influence of light and the hydrocelluloses become difficultly esterifiable. Berthelot and Gaudechon[4] have shown that nitrocellulose films when subjected to ultraviolet light decompose with the production of carbon dioxide, carbon monoxide, nitrogen, nitrous oxide and nitric oxide. It was also found[3] that acetone solutions of nitrocellulose became yellow and the viscosity was lowered on irradiation. The opinion was expressed that the decrease in viscosity was probably indicative of a depolymerization of the cellulose molecule. Solid ethyl cellulose was stable to light, but a solution showed a marked drop in viscosity. With solid benzyl cellulose, when exposed to ultraviolet light, a large amount of insoluble matter is produced. Mason and Rosevear[5] have studied the degradation of oriented cellulose structures by polarized ultraviolet light using the copper number as a means of measuring the degradation.

The authors thought it would be of interest to study the effect of ultraviolet light on solutions of methyl cellulose, using measurements of viscosity, osmotic pressure and copper number as means of determining whether or not degradation had taken place.

The methyl cellulose (Methocel M-340) was obtained from the Dow Chemical Company. This material is of 50 cp. viscosity type and has a methoxy content of 31.5%. The aqueous solutions of methyl cellulose were prepared

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(1) B. Rassow and W. Aehnelt, *Cellulosechem.*, **10**, 169 (1929).

(2) B. Rassow and F. Weber, Dissertation, Leipzig, 1929.

(3) L. Clement, C. Riviere and A. Beck, *Chimie et industrie*, Special No., 702-706 (March, 1932).

(4) D. Berthelot and H. Gaudechon, *Compt. rend.*, **154**, 201 (1912).

(5) C. W. Mason and F. B. Rosevear, THIS JOURNAL, **61**, 2995 (1939).