THE AMERICAN CHEMICAL SOCIETY.

IX

DYE SECTION

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Dye patents of the chemical foundation, incorporated: S. A. TUCKER. The paper deals with the classification of the dye patents owned by the company which forms the largest division of any class of its patents, and covers practically all classes of dyes. The method followed enables one to locate any patent either by the chemical constitution of the dye or its application. Patents actually licensed either by the Chemical Foundation or the Federal Trade commission are discussed at considerable length. A list of patents of which the Schultz number is known but which have not yet been licensed is given. The advantages in the form of license as issued by the Chemical Foundation are pointed out and the influence which the company may have on the American chemical industry is discussed.

Dyes for photographic sensitizing: W. F. MEGGERS and F. T. STIMSON. Illustrations are given of the photographic impression made by a continuous spectrum upon Seed's 23 plates before and after treating with typical photo-sensitizing dyes. Spectral transmission curves of the dye solutions and spectral sensitivity curves of photographic plates stained with the dyes are shown. Examples of the use of color sensitive photographic plates in aerial photography are exhibited and the importance of photo-sensitizing dyes to future developments in photography is emphasized.

Anthranilic acid, tests and purity of the commercial product: J. F. RAGSDALE. The melting point of anthranilic acid is found to be higher than that usually given in the literature. Since decomposition occurs on melting, certain precautions must be observed in taking the melting point. Various methods for determining the anthranilic content of the commercial product are discussed, and diazotation with standard nitrite solution is recommended. Several methods for standardizing the nitrite solution have been tried, and advantages and disadvantages of each are pointed out.

Ortho chlor para toluene sodium sulfonate—purity and tests of the commercial product: L. A. WATT. Ortho chlor para toluene sulfonate is one of the dyestuff intermediates now produced in quantity in this country. The impurities encountered in the commercial product are enumerated and a procedure for their detection and determination based on the relative solubilities in alcohol is suggested. Data obtained from the examination of both low grade and typical commercial products are given.

Uses of formic and oxalic acids in the dyeing industry: LANCELOT W. ANDREWS. For the acidification of dye baths, an acid should be selected having intrinsic strength enough to cause full utilization of the dye and fixation on the textile, but not having so great intrinsic strength as to injure the fabric. The intrinsic strength of the acids are determined by their electro-dissociation coefficients. It is shown by both theory and practise that formic acid is particularly well suited for use of the dyer and that its high dissociation constant and its low molecular weight, render its employment thoroughly economical. Formic acid offers the following advantages as compared with the mineral acids, or with acetic and other available organic acids: (1) No tendering of the textile, (2) greater evenness of dyeing, (3) better exhaustion of the dye, (4) better fixation on the textile, (5) brighter color, (6) better penetration, (7) economy. American manufacturers are now able to supply both formic and oxalic acids, and the mordant salts of these acids, with Al, Cr, Sn, Sb, etc.

Synthetic dyes as applied to chemico-therapy and microscopy: GEO. HEYL. Part 1. Medicinal Dyestuffs: (*A*) Theory of action. (*B*) Synthesis and pharmacological effect. (C) Classification of medical dyestuffs: (*a*) Eutherapeutic and dytherapeutics; (*b*) Dyestuff specifics (salvarsan, acriflavine, etc.); (*c*) External dyestuff antiseptic; (*d*) Dytherapeutics and parasiticidal action; Trypan blue, trypan red, naga red, methylene blue, etc.; (*e*) Neutral dyes and nerve cells; Methylene azur, eosine-azurs, etc., and neutral red. (D) General outline of preparation. Part 2. Microscopic Stains: (*A*) Theory of action (Ehrlich-Witt). (*B*) Classification. (*C*) Standardization.

Dye research: ROBERT E. ROSE. Research we must have—not a mere checking up of receipts, not a mere search for information which is known to others. We must graduate to real research, that is, enter the entirely unknown. Much of this type of research must be done in the universities, but under conditions of close cooperation with the industries. To do this latter, the industries must lose their intense secrecy, and open their doors—with proper safeguards—to the university men. Raw products, money, commercial organization, industrial chemists, all these we may have and yet fail if we have not real research.

The hydrogen exponent classification of indicators and some of its applications: I. M. Bernstein. (1) Definitions of terms used. (2) Determination of indicator constants: (*A*) Approximation method of Salessky; (*B*) colorimetric method; (*C*) Bjerrum's method. (3) Classification of indicators according to exponents: (*A*) Chart of same showing color changes; (*B*) comparison with Glaser's classification. (4) Application of classification of volumetric analysis: (*A*) Neutralization curves. (*B*) Selection and concentration of correct indicator. (*C*) Preparation of new indicators. (5) Application of classification to biological technic: (*A*) Determination of hydrogen ion concentration; (*B*) the selection of correct indicator for physiological solutions.

The analysis of aromatic nitro compounds by means of titanous chloride: F. L. English. The procedure for the analysis of aromatic nitro-compounds as recommended by Knecht and Hibbert (see "New Reduction Methods in Volumetric Analysis") has been modified and successfully applied to numerous typical nitro-compounds of the benzene series among which are *m* and *p*-nitranilines, *o*- and *p*-nitrophenols, *o*- and *m*-nitro-*p*-toluidines, two of the nitro-salicylic acid isomers, dinitrobenzene, toluene and xylene, trinitrotoluene and picric acid. The experimental figures given show the method to be accurate to about 0.1 per cent., total error. Results are given also to prove the inapplicability of the method in its present form to nitrochlor derivatives such as *o*- and *p*-nitrochlorbenzene and dinitrochlorbenzene, under-reduction resulting in the first two cases and over-reduction, probably at the expense of the chlorine atom, in the last. When the chlorine is in the side-chain, however, the reaction proceeds more nearly quantitatively as illustrated by *p*-nitrobenzyl chloride and dinitroxylyl dichloride (1–3–CH_2Cl–2–4–NO_2 benzene). The analytical procedure, as well as the preparation, standarization and storage of the volumetric solutions, is described in detail.

Some physical constants of pure aniline: C. L. Knowles. A sample of aniline was carefully purified by conversion to the oxalate, regeneration and repeated vacuum distillation. Physical constants were determined immediately without undue exposure to the air. Freezing and boiling point determinations were recorded by means of a recently standardized platinum resistance thermometer. The constants found are as follows:

Freezing point —6.24° C.
Boiling point 184.32–184.39° C. at 760 mm.
Specific gravity 15/15 1.0268.
Refractive index 20° C. 1.5850.

On exposure to the air aniline absorbs moisture very rapidly, taking up 2.4 per cent H_2O in 46 hours reducing the freezing point nearly 2° C. Indications are that the freezing point is the best criterion of purity which may be calculated by substitution in the following formula, (t) being the observed freezing point and (x) the per cent. aniline in the sample. $X = 108.79 + 1.41\ t$.

The absorption spectra of the nitric esters of glycerol: E. Q. Adams.

Tetramethylquinolines: L. A. Mikeska.

Naphthalene sulfonic acids. Some difficult soluble salts of naphthalene sulfonic acids: J. A. Ambler.

A method for the qualitative detection of some naphthalene sulfonic acids: J. A. Ambler.

Synthesis of s-Xylidine: H. L. Haller.

Alkali fusions. II. The fusion of sodium benzene disulfonate with sodium hydroxide for the production of resorcinol: Max Phillips and H. D. Gibbs.

A synthesis of thymol from p. cymene: Max Phillips and H. D. Gibbs.

The vapor pressure of phthalic anhydride: K. P. Monroe.

A new source of furfural and an investigation of the preparation and properties of "furfural green": K. P. Monroe.

The absorption spectra of the nitric esters of glycerol: Elliot Quincy Adams. Hepworth (*Jour. Chem. Soc.*, 115, 840–47 (1919)), from a study of the absorption spectra of the nitric esters of glycerol, concludes "(6) There does not appear to be any numerical proportionality between the number of hydrogen atoms of the hydroxyl groups displaced by nitro-groups and the degree of absorption for any particular dilution." A critical study of the results of Will (Ber. 41, 1107–23 (1908)), which have been accepted by Hepworth, indicates that his designations α- and β- for the mononitrates should be interchanged. Each nitrate radicle has an absorptive effect dependent on its location in the molecule, but independent of the presence of other nitrate radicles.

Tetra methyl quinolines: L. A. MIKESKA and E. Q. ADAMS. The dicyanines—a series of photosensensitizing dyes extending the sensitiveness of the photographic plate farther into the infra-red than any other known substances—requires as intermediates the quaternary halides of 2, 4 dimethylquinoline and 2, 4, 6-trimethylquinoline. These bases are made by condensing with paraldehyde and acetone—by a synthesis similar to that of Shraup—respectively aniline and *p*-toluidine. The xylidines give by this condensation tetramethylquinolines, of which only one has heretofore been prepared (and incorrectly named). Three of the six possible isomeric tetramethyquinolines have been prepared: 2, 4, 5, 7-; m.p. 59°; 2, 4, 6, 8-; m.p. 86° and 2, 4, 5, 8-. The preparation of the others is in progress.

Naphthalene sulphonic acids. I. Some difficultly soluble salts of certain naphthalene sulphonic acids: JOSEPH A. AMBLER. The preparation and properties of the alpha naphthylamine salts, and of the beta naphthylamine salts of the naphthalene alpha, beta, 1–5, 1–6, 2–6, and 2–7 sulphonic acids, and of ferrous naphthalene beta sulphonate are given. Crystallographic-optical properties as determined by E. T. Wherry are included. These salts are all difficultly soluble in water and possess characteristic optical properties.

Naphthalene sulphonic acids. II. A method for the qualitative determination of some of the naphthalene sulphonic acids: JOSEPH A. AMBLER and EDGAR T. WHERRY. It was found that the properties of the salts described in the preceding article can be used for a qualitative test for the naphthalene alpha, beta, 1–5, 1–6, 2–6, and 2–7 sulphonic acids. Naphthalene beta sulphonic acid is detected with ferrous chloride; the 1–5 sulphonic acid, with alpha naphthylamine hydrochloride in boiling water; the 2–6 sulphonic acid, with beta naphthylamine hydrochloride in boiling water; the alpha acid by the solubility of its beta naphthylamine salt in hot acetone; the 1–6 and 2–7 sulphonic acids, by the optical properties of their beta naphthylamine salts.

Benzene disulfonic acid from benzene monosulfonic acid: C. E. SENSEMAN. The well-dried barium salt of benzene monosulfonic acid is treated with sulfuric acid varying in concentration from 93–98 per cent. The temperatures for the various runs are 220°, 250° and 280°. The quantities of acid used range from 1½–8 mols to one mol of the free monosulfonic acid. The duration of the various experiments was from 8–10 hours. Vanadium pentoxide and sodium sulphate were tried out as catalysts. The progress of the reaction was determined in each case by removing a sample at the end of each hour and analyzing for the disulfonic acid. Without the use of a catalyst the highest yield obtained was 93.3 per cent. A yield of 98.2 per cent. was obtained when sodium sulphate was used as a catalyst.

Synthesis of s-xylidine: HERBERT L. HALLER and ELLIOT Q. ADAMS. S-xylidine was synthesized (1) from mesitylene—which was oxidized to mesitylenic acid; changed to the amide; and finally converted by means of Hofmann's reaction to *s*-xylidine; (2) from *m*-4 xylidine by successive acetylation, nitration, saponification and deamination; and reduction. In the latter procedure the saponification and deamination were carried out in one step. Acetyl derivatives of the xylidine obtained by the two methods were compared, and their melting points found to be the same, 139.6°–140.2° (corr.). The optical properties also were found by Dr. E. T. Wherry to be identical.

Alkali fusions. II. The fusion of sodium benzene m-disulphonate with sodium hydroxide for the production of resorcinol: MAX PHILLIPS and H. D. GIBBS. Although the process of making resorcinol by the fusion of sodium benzene *m*-disulphonate with sodium hydroxide has been in use for a considerable number of years, nevertheless, there appears to be no agreement as to what are the proper conditions for conducting the fusion in order to obtain the highest yield of resorcinol. Using an apparatus especially suited for this work, a study was undertaken for the purpose of ascertaining the optimum conditions for conducting the alkali fusion. The problem resolved itself into a study of the four following factors: (1) Ratio of sodium hydroxide to the sodium benzene *m*-disulphonate; (2) the proper fusion period; (3) the proper fusion temperature; (4) effect of the addition of water to the sodium hydroxide upon the yield of resorcinol. The results obtained indicate that 310° is the best fusion temperature, two hours the best fusion period, 14 to 16 moles sodium hydroxide to one mole sodium benzene *m*-disulphonate the best fusion mixture, and that water when present in the fusion mixture tends to reduce the yield of resorcinol.

A synthesis of thymol from p-cymene: MAX PHILLIPS and H. D. GIBBS. *p*-cymene, an aromatic hydrocarbon, although long known to chemists, has recently attracted considerable attention because of the fact that it is obtained in rather large quantity as a by-product in the spruce pulp industry. Thymol, which is of considerable commercial importance and which bears the same relation to *p*-cymene as does phenol to benzene, can not be obtained from *p*-cymene by the ordinary methods of getting a phenol from its corresponding hydrocarbon. However, by using the following rather indirect method the synthesis of thymol was accomplished: *p*-cymene was nitrated and the compound with the nitro group in the position ortho to the methyl group was obtained. This compound was reduced to the corresponding amino *p*-cymene or cymidine, which when sulphonated gave cymidine sulphonic acid, the sulphonic group entering the position ortho to the isopropyl group. The amino group of cymidine sulphonic acid was then removed through diazotization and subsequent reduction with alcohol and copper powder. The cymene sulphonic acid thus obtained was converted into its sodium salt and the latter when fused with sodium hydroxide was converted into thymol.

The vapor pressure of phthalic anhydride: K. P. MONROE.

The preparation of furfural: K. P. MONROE. Corn-cob adhesive prepared according to the method of La Forge and Hudson (*J. Ind. Eng. Chem.*, 10 (1918, 925) by extracting corn-cobs with water under pressure at 150° C. is an excellent source for furfural, since the gums so obtained are rich in pentosan and yield 26 per cent. of pure furfural. The essential improvements over the previously published methods of obtaining furfural from pentosan containing material are (1) removal of furfural from the reaction mixture by a rapid current of steam during the hydrolysis by 25 per cent. H_2SO_4; (2) separation of furfural from the dilute aqueous solution which constitutes the distillate by distillation with the acid of a fractionating column. Uses for furfural in the industries and arts are outlined; among these are the preparation of: hard resins similar to the well-known "Bakelite," soluble resins which may find application in the varnish trade, a series of dyes which may be obtained by condensation with various coal-tar products.

The vapor pressure of phthalic anhydride: K. P. MONROE. The vapor pressure of phthalic anhydride was determined by the static isoteniscope method of Smith and Menzies (*J. Am. Chem. Soc.*, 32 (1910), 1412–59). The following equation, of the type obtained by integration of the Clausius-Clapeyron equation with simplifying assumptions, was found to express the results:

$$(1) \qquad \log_{10} p = 7.94234 - \frac{2823.5}{T}$$

where p = vapor pressure in millimeters of mercury and T = absolute temperature. The molar latent heat of vaporization was calculated to be 12,910 colories, while the value 13.6 was obtained for the entropy of vaporization divided by R (the gas constant) at the temperature (near 218°) at which the concentration of vapor is 0.00507 mole per liter. According to the criterion of Hildebrand (*J. Am. Chem. Soc.*, 37 (1915), 970), this indicates phthalic anhydride to be a *normal* liquid.

The present independence of American synthetic dyes and how it was accomplished: ROBERT E. HUSSEY. Prior to the war all of the biological dyestuffs used in the bacteriological laboratories and in the laboratories of public health came from Germany. The two chief difficulties upon the cessation of imports that confronted the American manufacturer were lack of raw supplies and lack of accurate information as to their manufacture. All of these dyes must be absolutely uniform and standardized as certain arbitrary amounts are used in certain dilution to attain specific results. The army had to be supplied. Quantity production took place and, after much experimentation, this experience has now made it possible to supply scientific dyes equal and in some cases, superior to those formerly imported. Investigators should mention that American dyes were used to obtain their result for by this method proper encouragement to this industry would be given.

CHARLES L. PARSONS,
Secretary

(*To be continued*)

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