

May number of the *Journal of General Physiology*. Former values were lower since the solutions contained less than 1 g. in 100 cc., usually 0.8 g., as was pointed out in a paper published in January, 1921, in the same *Journal*.

I have recently shown that the osmotic pressure of a gelatin solution of a given hydrogen-ion concentration is not a constant, since it diminishes on standing on account of the formation of aggregates.

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### NOTES.

**Synthesis of Indigo from Fumaric Acid and Aniline.**—In the "Text-Book of Dye Chemistry" by G. von Georgevics and Grandmougin<sup>1</sup> there is the statement that indigo has never been obtained by fusion with potash followed by air oxidation from dianilido-succinic acid  $C_6H_5.NH.CH(COOH)CH(COOH).NH.C_6H_5$ . In the course of some work on the compounds derived from maleic acid the following experiments were made which show that appreciable yields of indigo may be obtained from this compound.

**Preparation of Dibrom-succinic Acid.**—The method given by Michael<sup>2</sup> was used. Thirty g. of fumaric acid, 41.4 g. of bromine, and 26 cc. of glacial acetic acid were heated in a sealed tube at 100° for 7 hours. The contents of the tube were washed into an evaporating dish with a little acetic acid and evaporated to dryness. The average yield on three runs was 96.5%.

For the preparation of dianilido-succinic acid the method given by Reissert<sup>3</sup> was followed. The yields were 37%, 38.7% and 41.5% of the theoretical.

**Fusion of Dianilido-succinic Acid to Indigo.**—Vorländer<sup>4</sup> recorded that he secured indigo in 3 out of 40 or 50 trials by fusing the above acid with potassium hydroxide. No yields were given. The fusion of the free dianilido-succinic acid by us with a molecular mixture of potassium and sodium hydroxide (9.6 parts to 1 part of acid) in a small crucible at 450° for 1½ hours followed by air blowing failed to give a trace of indigo. Similar negative results were obtained in a closed agitated pot with the mixed caustic. However, indigo was obtained by the following procedure. A molecular mixture (300 g.) of potassium and sodium hydroxides was dehydrated at 450° for 2½ hours in a closed agitated iron pot. Thirty g. of sodamide was then added and a stream of dry ammonia passed through

<sup>1</sup> Scott, Greenwood and Co., London, 1920. Trans. from 4th German ed. by F. A. Mason.

<sup>2</sup> Michael, *J. prakt. Chim.*, [2] 52, 295 (1851).

<sup>3</sup> Reissert, *Ber.*, 26, 1763 (1893).

<sup>4</sup> Vorländer, *Ber.*, 27, 1604 (1894).

the pot. To the melt 25 g. of the sodium salt of dianilido-succinic acid was added. The temperature was held at 230–240° for 1½ hours. The melt was dissolved in water and blown with air. Indigo precipitated and was filtered off. The yield was 11.5 g. or 60.4% of that calculated on the basis of 100% indigo from pure (100%) dianilido-succinic acid, or 25% on the fumaric acid added.

This indigo was 96.5% pure by the method of Bloxam<sup>5</sup> and showed satisfactory dyeing qualities.

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**The Occurrence of Terpin Hydrate in Nature.**—Terpin hydrate, (C<sub>10</sub>H<sub>20</sub>O<sub>2</sub>.H<sub>2</sub>O), a well crystallized substance, has long been known as a product of the synthetic laboratory. It is easily prepared by allowing turpentine oil to stand in the air in contact with water for a long time or more rapidly by adding nitric acid and alcohol to the mixture. It seems strange, then, that it should not have been formed by natural agencies, yet until recently it was unknown in nature. In October, 1920, the writer described a crystalline substance, flagstaffite, found in buried pine logs, giving the result of chemical analyses, molecular weight determinations and crystallographic measurements.<sup>1</sup> At that time he was unable to find any natural or synthetic product that corresponded to it, but later, on the suggestion of Dr. Francis D. Dodge of Brooklyn, N. Y., careful comparisons were made with terpin hydrate with the result that both crystallographically and chemically they were found identical.<sup>2</sup> The discovery of this substance in logs buried at least 500 years as shown by tree rings in stumps still rooted in the debris, adds a new mineral species, while its identity with a well-known synthetic product is of general interest.

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**The Action of Halogens on Aceto-acetic Ester.**—The action of chlorine and of bromine on aceto-acetic ester has been the subject of many investigations and of considerable controversy. In a series of researches extending from 1890–4 Hantzsch finally proved, by a method that is both elegant and conclusive, that the product obtained by passing chlorine into the ester is an  $\alpha$ -chloro derivative, while that obtained by adding bromine to solutions of the ester is a  $\gamma$ -bromo compound. Hantzsch also discovered that in the presence of hydrogen bromide, the  $\alpha$ -bromo ester obtained by

<sup>5</sup> Bloxam, *J. Soc. Chem. Ind.*, **25**, 735 (1906).

<sup>1</sup> Guild, *American Mineralogist*, **5**, 155 (1920).

<sup>2</sup> Guild, *ibid.*, **6**, 133 (1921).