

in some of the nitrogenous material of the seed, thereby making available free amino groups or free ammonia which could then react with gossypol to form diaminogossypol.

High temperatures during storage have been shown to increase the color of the oil produced from such seed. It had been previously postulated (7) that gossypurpurin and its decomposition products may be responsible for the dark colors of the expressed crude oils. In this investigation it was confirmed that high temperatures during storage of the seed increased the content of gossypurpurin and this pigment could be one of the major components contributing to the dark colors of the expressed cottonseed oils.

The non-acidic pigment(s), containing diaminogossypol, which are found more abundantly in cottonseed after storage for long periods of time at high temperatures, may account for some of the increased color observed in refined cottonseed oil. During alkali-refining gossypol is removed, but the yellow non-acidic pigment(s) are not removed. Isolation and identification of these non-acidic pigments and other conversion or decomposition products of gossypol and gossypurpurin may make possible a more rational control of the color of finished cottonseed oils.

#### Summary

Three pure-bred varieties of cottonseed, *G. hirsutum*, which were planted and grown under similar environmental conditions were stored at 38°, 77°, and 85°F. After determining the initial contents of lipids, nitrogen, moisture, gossypol, and gossypurpurin each lot of seed was stored at the different temperatures and analyzed periodically with respect to changes in pigmentation.

The content of gossypurpurin was found to increase during storage in all of the samples. Its increase was proportional to the temperature and length of storage. On the other hand, gossypol decreased during storage of all samples.

The antimony trichloride test for gossypol was found to be applicable only to extracts prepared from fresh cottonseed. During storage of the seed another yellow-colored pigment(s) developed which could be separated from gossypol by alkaline extraction of the original chloroform extract of the stored seed. The alkali extractable portion of the chloroform extract gave a red-colored antimony trichloride reaction product characteristic of gossypol.

It is postulated that at least a fraction of the non-acidic pigment(s) in the crude chloroform extracts obtained from stored cottonseed is diaminogossypol.

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## A Convenient Heating Apparatus for Isomerization of Oils for Spectrophotometric Analysis\*

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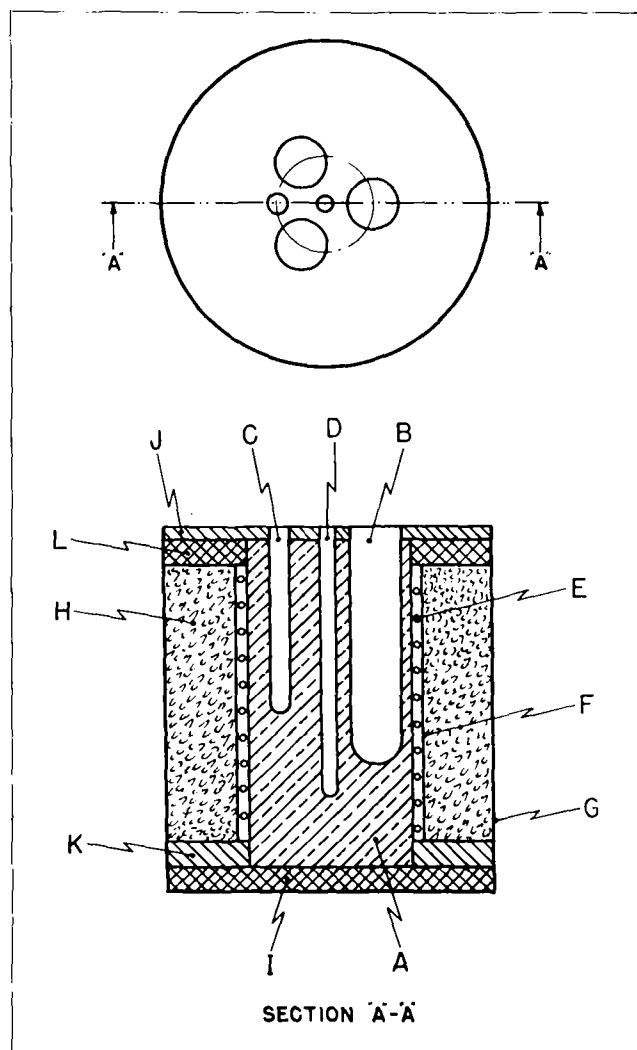
THE alkali isomerization of fatty materials during spectrophotometric analysis for polyunsaturated constituents has been carried out in constant temperature baths containing bath wax (1) or mineral oil (2). These baths have disadvantages from the points of view of cleanliness, fumes, and fire hazard. An alternative heating apparatus is described which is rapid in operation and convenient.

The apparatus (Fig. 1) consists of an electrically heated cylindrical brass block  $3\frac{1}{8}$  in. in diameter and 6 in. long (A), drilled to hold three 6 x 1 in. matched test tubes at a depth of  $4\frac{1}{2}$  in. (B), a mercury thermoregulator (C) and a thermometer (D). (A larger cylinder could be used to accommodate

more test tubes.) The heating element, 500 watts, (E) is a double winding of No. 20 gauge Chromel wire with the windings insulated from each other by porcelain cement. The element is insulated from the brass block (A) by a layer of asbestos paper (F). To reduce heat loss to the surrounding air the unit is sealed inside a No. 10 can (G) insulated around the circumference with glass wool (H), at the bottom with a half-inch layer of insulating board (I), and at the top with a  $\frac{3}{16}$  in. sheet of asbestos (J) with openings to match the holes in the block. Two rings of  $\frac{1}{2}$  in. insulating board (K and L) center the block and keep it from shifting inside the can.

The thermoregulator is connected to a relay, which may be by-passed by means of a switch. A Variac is

\*N. R. C. No. 1963.



used to adjust the amount of current passing through the heating element.

Owing to the relatively slow transfer of heat from the heating block to the test solutions, it is necessary to hold the block at a slightly higher temperature than that desired in the tubes. The transfer of heat was improved slightly by coating the insides of the holes in the block with heat resisting flat black enamel, but there was still a temperature differential between the block † and the solutions. For this apparatus a block temperature of  $181^{\circ} \pm 0.2^{\circ}\text{C}$ . maintained a temperature of  $180^{\circ} \pm 0.2^{\circ}\text{C}$ . in the tubes containing the isomerization solutions, with a temperature difference of less than  $0.1^{\circ}\text{C}$ . among the three tubes. A constancy of  $\pm 0.5^{\circ}\text{C}$ . has been found satisfactory for the isomerization reaction (1). The block came to  $181^{\circ}\text{C}$ . in 30 min. and the solutions came to  $180^{\circ}\text{C}$ . in 25 min. after the tubes were inserted in the heated block. The solutions could be brought to  $180^{\circ}\text{C}$ . in about 15 minutes if the thermoregulator were bypassed for one to two minutes immediately after the tubes were inserted.

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† Although a brass block was used because brass is easy to drill, aluminum has a higher heat capacity and thermal conductivity; the differential between the temperatures of the block and sample might be reduced somewhat if aluminum were used.

## Polymerization of Drying Oils. V. Further Observations on the Reaction of Unsaturated Dibasic Anhydrides With Methyl Linoleate<sup>1</sup>

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THIS paper reports the results of experiments on the condensation of methyl linoleate with itaconic and citraconic anhydrides and the reaction of the condensation products with ethylene diamine. Experiments on the condensation of methyl linoleate and maleic anhydride in the presence of dimethylaniline are also described.

In a previous communication (5) it was shown that the reaction product of one mole of methyl linoleate and two moles of maleic anhydride could be separated

into two components. One component, volatile in the molecular still, appeared to be a monoadduct containing one mole of methyl linoleate and one of maleic anhydride. The other component, non-volatile in the molecular still, had properties indicating that it was a polymeric adduct of two moles of methyl linoleate and three of maleic anhydride. This polymeric adduct was found to give gelled products when treated with ethylene diamine.

The experiments with itaconic and citraconic anhydrides were undertaken with the expectation that these anhydrides, considered as substituted maleic anhydrides, would show a reduced reactivity towards methyl linoleate. It was thought that such lowered reactivity might prevent the formation of polymeric adducts and increase the yield of monoadduct.

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