Small amounts of chromium may be detected and estimated by means of diphenylcarbazide.

Small amounts of other metals, especially iron, aluminium, copper and silica which are apt to be found in the ash of fats, do not interfere in this reaction.

THE PROCTER & GAMBLE CO.,
IVORYDALE, OHIO

ACTION OF FATTY ACIDS AND OILS ON A PHOTOGRAPHIC PLATE[1]

BY WALTER F. BAUGHMAN AND GEORGE S. JAMIESON

Photographers know that a developable impression can occur on a photographic plate which never has been exposed to the light. Old plates frequently show black borders after development and markings are sometimes observed on "daylight" films. The printed identification marks on the black paper of these films have been known to register themselves on the negative.

Russell[2] has demonstrated that many substances produce on a photographic plate results very similar to those produced by light. Some of the substances mentioned by Russell are magnesium, cadmium, zinc, nickel, aluminium, lead, bismuth, tin, cobalt, antimony, wood, leaves, seeds, roots, bulbs, petals of flowers, linseed oil, olive oil, terpenes and resins. He found starch, cellulose, gum, sugar, pith, pollen and paraffin oils to be inactive.

These active substances differ widely in character but their action on the plate is apparently the same except for intensity. With some substances a developable impression can be obtained in an hour; with others 18 or 20 hours are necessary. No visible change is produced on the plate before it is developed and the development is the same as for an ordinary photograph. It is not necessary to have the substance in contact with the plate. Russell found that with some substances the action would travel through a distance of 200 mm., although in most of his experiments the plate was within several millimeters of the substance.

The object of the present investigation was to examine the photographic action of fatty oils. The photographic plate was exposed to the oil in a desiccator jar so as to preclude any possible action from fumes that might be in the atmosphere. The jar was placed in a box, which was painted black inside and provided with a tightly fitting lid, so that the dark room in which the box was placed could be entered and left without affecting the experiments. Uncovered petri dishes holding about 35 g.

[1] Presented before Am. Chem. Soc., Washington Meeting, April, 1924.

[2] Proc. Royal Inst. of Great Britain, **16,** 140 (1899–1901); Proc. Royal Soc. of London, *Biol. Sci.*, **78,** 385 (1906) and **80,** 376 (1908).

of oil, which came within two or three millimeters of the top, were used for each experiment. Pieces of white blotting paper with designs cut in them were laid across the dishes and the photographic plates were placed on top of the blotting paper.

Freshly expressed peanut, corn, cottonseed, linseed and chinawood oils produced no pictures when plates were exposed to them for 18 hours at room temperature. After these oils had been exposed to the sun for five or six hours, however, they did produce pictures of the designs cut in the blotting paper. Peanut oil produced a rather faint picture; corn and cottonseed oils, much sharper ones. When corn and cottonseed oils were used, the action went through the blotting paper and produced a dark disk on the plate. With linseed oil a very sharp picture and a dark disk were obtained. Chinawood oil produced only a faint picture. Several miscellaneous oil samples that had been in the laboratory for various lengths of time were placed with photographic plates. Perilla oil, six years old, produced a sharp picture and a faint disk; sesame oil, six months old, a faint picture; olive oil, three years old, a sharp picture and a disk; U. S. P. castor oil, a sharp picture and a dark disk; commercial coconut oil, a sharp picture and a dark disk. A sample of butterfat, which was known to be 26 years old, gave a sharp picture and a very faint disk. Commercial hydrogenated sesame oil with an iodine number of 27.2 (the iodine number of sesame oil is 110) gave no picture but after being exposed to the sun for five or six hours it produced a picture of medium intensity.

The following tests were made to determine whether there is any difference between the photographic activity of saturated and unsaturated fatty acids. Neither palmitic acid (m. p. 62.5, prepared in this laboratory) nor stearic acid (Kahlbaum) gave a picture, even after being exposed to the sun for five hours. Oleic acid (Kahlbaum) that had been kept in a brown bottle in a dark cupboard for several years, upon being placed with a plate for 18 hours gave a faint picture, but after exposure for four or five hours gave a very dark picture and disk. The sun-exposed oleic acid required only two and one-half hours to produce a medium dark image. The saturated and unsaturated acids were separated from an inactive refined cottonseed oil by the lead salt-ether method. The saturated acids gave no picture after exposure to the sun. The unsaturated acids, however, showed even more activity than the oleic acid. When placed with a plate for 18 hours, they produced a faint image before being activated by the sun and after being in the sun for five hours, a disk so black that the image was almost completely obscured. The sun-activated unsaturated acids produced a medium dark image in one and one-half hours. It is evident therefore that the photographic activity of fatty oils is connected with the unsaturated acids.

The activity of an oil or fatty acid is destroyed or greatly decreased by heating to approximately 120° for several hours. The activity can be transferred to a certain extent. Blotting paper placed over very active oils becomes permeated with the active substance and then is capable of affecting a plate.

Russell's experiments indicate that this photographic action of certain substances is produced by a vapor rather than by any form of radioactivity. He found that the action would pass along a glass tube, even when it was bent at right angles, that it could be swept out of a tube by a slow current of air and that it did not affect an electrical field. He attributed the activity to the formation of H_2O_2 and states that all active metals have the property of producing H_2O_2 in the presence of moisture, that terpenes in the presence of moisture and air cause the formation of H_2O_2 and that every result obtained by exposing a plate to a metal or organic body can be exactly imitated by using H_2O_2. He found that a picture could not be produced in an atmosphere of CO_2.

The authors have found that an oil containing 0.0016% H_2O_2 will produce a very dark image and a medium dark disk during an 18-hour exposure and that an oil containing 0.0002% H_2O_2 will produce a medium dark image but no disk. The active substance leaves the oil slowly and whatever the nature of the substance causing the photographic action, the amount that comes off the oil during 18 hours is very small.

The following tests were made while attempting to establish the identity of this substance:

Blotting papers saturated with a solution containing KI, starch and a little $FeSO_4$ were laid across petri dishes, containing the most active oils, in desiccator jars and allowed to remain for 18 or 20 hours. Small beakers containing a few cubic centimeters of water were placed in the jars to keep the blotting papers moist. The unsaturated acids of cottonseed oil produced a reddish purple disk and the other less active oils gave fainter disks or none. Tests were made in a similar way with titanium sulfate, which is given by Treadwell and Hall as a test for distinguishing between hydrogen peroxide and ozone. In this case the unsaturated acids produced a distinctly yellow disk. The others evidently were not active enough to give a coloration. The vapor given off by cottonseed oil unsaturated acids was also tested with a blotting paper saturated with a solution containing ferric sulfate and potassium ferricyanide. At the end of 18 or 20 hours there was a blue disk on the paper showing that there had been a reduction to ferric ferrocyanide. These results are strong evidence that the active substance is hydrogen peroxide.

Summary

Russell has shown that many substances, such as certain metals, wood, leaves, roots, bulbs and resins, have the property of producing a develop-

able impression on a photographic plate when placed in proximity to it in the dark. He believed that the active substance is hydrogen peroxide. The present investigation shows that freshly expressed vegetable oils or fats do not have this property but after they have been exposed to the sun for several hours they become active. The saturated fatty acids are inactive, even after exposure to the sun. On the other hand, the unsaturated fatty acids are faintly active before exposure to the sun and after such exposure become intensely active.

Heating to approximately 120°C. for several hours destroys or greatly decreases the activity. Blotting paper placed over very active oils becomes permeated with the active substance and capable of affecting a plate.

The substance that is given off by an active oil will liberate iodine on a test paper saturated with a solution containing potassium iodide, starch and a little ferrous sulfate. It will turn a paper saturated with titanium sulfate, yellow, and a paper saturated with a solution containing ferric-ferricyanide, blue, showing that there has been a reduction to ferric-ferrocyanide.

These results confirm Russell's opinion that the substance is hydrogen peroxide.

This investigation was proposed by Dr. C. A. Browne, Chief of this Bureau, and the authors are indebted to him for many helpful suggestions.

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AN APPARATUS FOR APPROXIMATE OR COMPARATIVE MELTING POINTS OF FATS, WAXES AND PETROLEUMS

By Hoyt Stevens

This apparatus consists of the ordinary hand-stirred melting-point bath of paraffin oil and thermometer and in addition a one inch titer tube or short test-tube equipped with a two-hole stopper which has a small groove along one side to prevent possible pressure when subjected to heat.

The holes in this stopper are bored, as nearly as possible, equal distances from the circumference of the stopper and about one-eighth inch apart. They are made to accommodate a thermometer and a glass rod (slightly smaller than the thermometer) whose bottom end is cut off square and left sharp.

The sample in case of solids such as beeswax, carnauba wax, paraffin, spermacetti, stearic acid, etc., is melted on a water bath and the bottom end of the rod dipped in about one-half inch and immediately withdrawn. By holding the rod horizontally and rotating while cooling, a uniformly thin film is produced. The small drop adhering to the bottom of the rod is scraped