sumed. Since the region adjacent to the surface of the metal is alkaline, the acid cannot aid in this cleaning. Meanwhile, the rate of cleaning of surface with which alcohol is not reacting decreases, due to the decrease in the concentration of acid. When equal areas of the metal are being cleaned and covered in the same period of time, the clean area will have reached a maximum, and the maximum rate of reaction will be observed. The higher the initial concentration of an acid, the larger will be the quantity of acid consumed during the induction period and consequently the area of clean surface. This is what happens, as can be seen from the data in Tables III and VII. From the point of maximum reaction onward surface is covered more rapidly than cleaned.

The observed rate of reaction at any time depends on the area of clean surface. This, in turn, appears to be related to the concentration of ethylate ion adjacent to it. We should expect this to be so, since the concentration of ethylate ion next to the surface should be an important factor in determining the amount of magnesium hydroxide which forms on the metal due to the reaction with water. From the results of the experiments to determine the influence of temperature and the rate of stirring we should conclude as was pointed out previously, that the rate of disappearance of ethylate ion from the surface by transport of acid and ethylate ion only partially determines the concentration of ethylate at the reaction interface. It also depends on the actual rate of the chemical reaction between the magnesium and the alcohol molecules. That is, the two rates do not differ sufficiently in magnitude for one to be the sole rate-determining factor.

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Summary

1. It was found that magnesium can displace hydrogen from the molecules of ethyl alcohol without the intermediate formation of solvated proton.

2. When magnesium dissolves in solutions of acids in ethyl alcohol the predominant reaction is between the metal and the alcohol. The production of ethylate ion is sufficiently rapid to prevent other acids from reaching the metal.

3. The observed rate of reaction depends directly on what portion of the measured surface of the metal is available for reaction. This is related to the concentration of ethylate ion at the reaction interface, which is determined by two processes whose velocities do not differ sufficiently for either of them to be the sole rate-controlling factor. They are the actual rate of the chemical reaction between the metal and alcohol and the rate of removal of ethylate ion from the reaction interface by neutralization and transport.

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NOTES

Ultramicroscopic Examination of Mixed Films

BY FREDERICK M. FOWKES, ROBERT J. MYERS AND WILLIAM D. HARKINS

The presence of a paraffin oil, such as nujol, in an expanded film formed by a fatty acid, such as myristic or pentadecylic acid, has a surprisingly great effect upon the pressure–area relations, as found by Myers and Harkins [R. J. Myers and W. D. Harkins, *J. Phys. Chem.*, **40**, 959 (1936); W. D. Harkins and R. J. Myers, THIS JOURNAL, **58**, 1817 (1936)]. This fact suggests that even if some of the paraffin oil is present in the form of lenses, a part remains mixed with the monomolecular film of acid. Myers and Harkins were unable to find any lenses visible to the naked eye in most of the mixed films investigated by them. In order to determine whether microscopic lenses are present, somewhat similar work has been done in which the pressure–area relations were determined by the Wilhelmy method and simultaneous observations of the structure of the film were made by the use of a dark field condenser and a microscope, as in the work of Zocher and Stiebel [*Z. physik. Chem.*, **147A**, 40 (1930)].

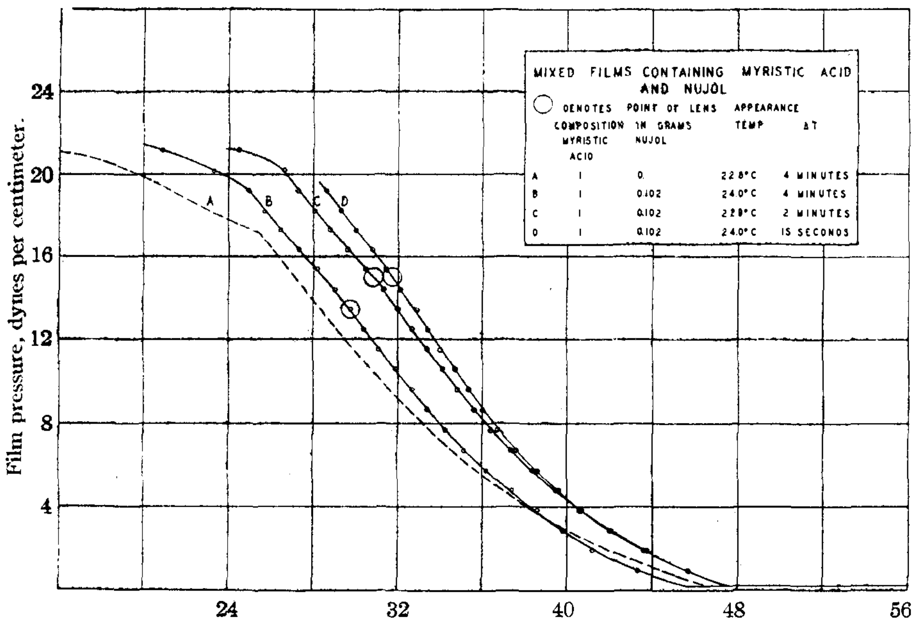

Fig. 1.

Mixtures of one part by weight of nujol to two parts of stearic, myristic, pentadecylic or oleic acids exhibit many oil lenses from gaseous film pressures up through collapse pressures. The average lens diameter in these films is about 1–2 μ and the lens concentration on an expanded film is of the order of 2000 lenses per sq. mm.

All films which contain a larger ratio of the paraffin oil to fatty acid give oil lenses, the lenses increasing in size as the relative concentration of the oil increases.

However, when mixtures which contain 0.3 or less parts of the paraffin oil to one part of fatty acid are examined, no lenses appear until the film is compressed to a certain critical pressure. At these points the lenses appear suddenly, their diameters seem to be less than 1 μ, and their concentration is of the order of 2500 lenses per sq. mm. If the pressure is decreased one or two dynes per cm. the lenses disappear, but reappear as before upon recompression. The force–area curves with nujol–myristic acid mixtures on 0.01 *m* hydrochloric acid show the dependence of the appearance of the lenses on film composition, film pressure and rate of compression. It probably depends also on the nature of the substrate.

The apparent compressibility of the film increases as the time of compression is increased (Fig. 1), but lenses first appear at areas which are largest for the most rapid compression. In both figures the line of dashes represents pure myristic

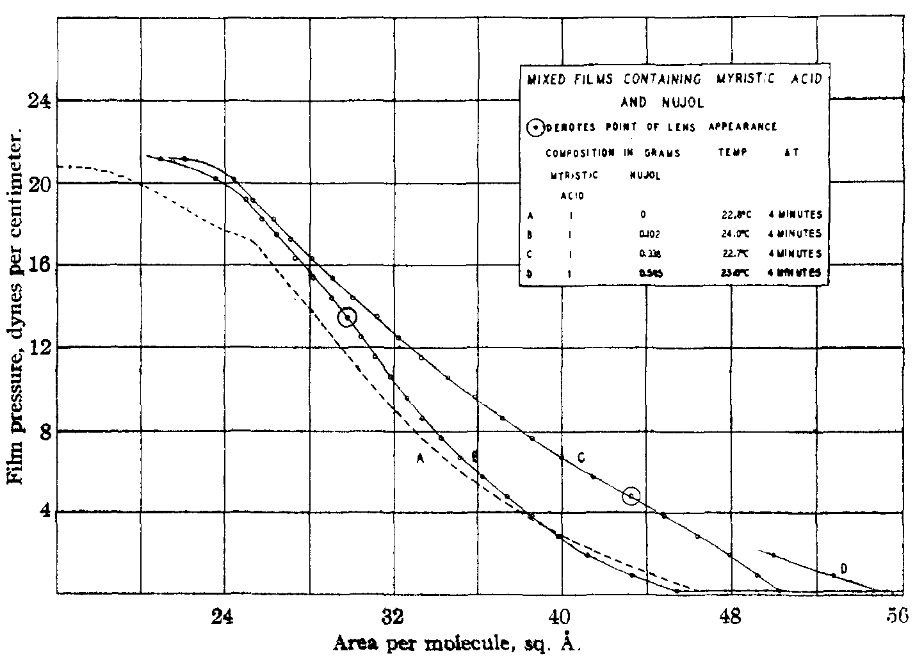

Fig. 2.

acid. All areas for the mixtures refer to the area per molecule of the acid, without reference to the amount of paraffin oil present.

From Fig. 2 it is obvious that at areas at which no lenses are visible, if the molecules of acid were to be oriented as in a condensed film, the total area would be more than sufficient to allow every molecule of the paraffin oil to be in contact with the water, but it is not suggested that the orientation is of this type. The presence of the oil causes these films to occupy larger areas, and Myers and Harkins have shown that larger amounts of oil expand the film at low pressures, but more greatly condense it at high pressures.

Thus it appears that uniform mixed films composed of fatty acids and liquid hydrocarbons may exist but these films are transformed at definite film pressures to composite films with lenses of hydrocarbon oil.

An investigation of these phenomena is in progress. An important feature revealed in this work is that the appearance of the lenses does not give rise to a discontinuity in the pressure–area curves.

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Protein Content of the Bark of Black Locust, *Robinia Pseudacacia*

BY D. BREESE JONES AND SAMMIE PHILLIPS

The observations here recorded relate to the surprisingly large quantity of protein in the bark of the common black locust tree. Protein is a well-recognized constituent of most plants and animal tissues, but as far as known the black locust is the only tree from the bark of which protein has been isolated and studied.

In 1899, Power and Cambier[1] demonstrated that the protein of the black locust tree was responsible for the poisoning of horses which had gnawed the bark of this tree. Later, other investigators[2–4] found that hypodermic injections of a solution of this same crude protein preparation produced an alteration of the kidneys producing a nephritis, and that even in great dilutions it agglutinated the red corpuscles of the blood of many different animals. Several instances are recorded[5] where both people and animals have been poisoned by the bark of the locust tree.

In the work of the authors referred to only the crude protein coagulum was used. No attempt was made to study the chemical and physical properties of the bark proteins or to determine the amount of protein in the bark. In 1925, Jones and Gersdorff[5] found that the dried inner bark collected from two locust trees in Maryland contained 17.5% crude protein. This protein was found to consist chiefly of a globulin, albumin and a proteose. The physical properties and composition of the proteins isolated were similar to those of most vegetable and animal proteins. They contained practically the same assortment and proportions of amino acids as found in most proteins.

Occasion was recently had to examine the bark from a number of black locust trees grown in different localities. This bark was collected[6] in Ohio and Indiana from trees ranging in age from seven to ten years. The outer brown, suberous portion of the bark was carefully removed. Only the inner, light colored portion was employed. The latter was allowed to dry by exposure to the air, and then was ground to a coarse powder in a mill. Moisture in the ground bark was determined by heating for twenty-four hours at 110°. Nitrogen in the samples was determined by the Kjeldahl method, and the crude protein calculated by multiplying the percentage of nitrogen by the conventional factor 6.25. The percentages given in Table I are based on moisture-free material.

The quantity of protein found covers a rather wide range. The average, 21.5%, is, however, considerably higher than that previously found in this Laboratory when working with the bark from the trees grown in Maryland. This difference may be due to the fact that the barks were collected at different seasons of the year. The bark from the Maryland trees was collected about the middle of August, while that from the

(1) F. B. Power and J. Cambier, *Pharm. Rundschau*, **8**, 29 (1890).

(2) C. Lau, "Uber vegetabilische Blut-Agglutinine," Inaugural dissertation, Rostock, 1901, p. 64.

(3) R. Kobert, *Landw. Vers.-Sta.*, **79–80**, 97 (1913).

(4) P. Ehrlich, *Klin. Jahrb.*, **6**, 315 (1898).

(5) D. B. Jones, C. E. F. Gersdorff and O. Moeller, *J. Biol. Chem.*, **64**, 655 (1925).

(6) The samples were collected under the supervision of Dr. Ralph C. Hall of the Bureau of Entomology and Plant Quarantine, to whom grateful acknowledgment is made. Some locust trees are seriously damaged by the locust borer. Other trees seem to be resistant to the attacks of this insect. Determinations of protein in the bark of resistant and susceptible trees were made with the idea that there might be a correlation between immunity to borer attack and the quantity of protein in the bark. No such correlation was found, however.