water is merely a confirmatory test, a high solubility indicating high alcohol content, although the presence of ethyl lactate increases the solubility in water. There would be no difficulty, however, in distinguishing between alcohol and ethyl lactate by examination of the boiling range curve. Solubility in three volumes of saturated sodium chloride solution gives an indication of the amount of methanol, ethyl alcohol, and acetone present.

Correlation and Evaluation of Results

The correlation of the results of the various tests is by no means easy. The greatest help is a fund of experience gained by working with solvents in various mixtures. The boiling range indicates which of the various solvents may be expected and in combination with the saponification value one can estimate quite accurately what materials are present and how much of each.

Exact figures for the composition of a lacquer cannot be expected to result from the usual examination such as here outlined. For instance, no known method will distinguish between butyl acetate and amyl acetate with the accuracy that we can distinguish between butyl acetate and butyl alcohol. For this reason the composition of a lacquer as the result of an analysis can best be expressed as varying within certain limits.

The total hydroxyl group can be ascertained by acetylization, but the method is useless as a means of determining whether the actual constituents are monatomic alcohols or hydroxy esters such as ethyl lactate. Here again the boiling range curve will help in making correct deductions.

Special Tests

Special analytical procedures can be applied in the case of certain solvents, which serve as definite measures of the amounts of these various constituents. For example:

METHANOL—Chapin-Elvove test, or the prussic acid method
ALKYL CARBONATES—Determination of the carbonate formed by saponification
ALKYL LACTATE—Oxidation with permanganate and determination of the acetaldehyde formed
ALKYL OXALATES—Saponification and determination of oxalate radical
ACETONE—Messenger or hydroxylamine method

ORGANIC ACIDS—It sometimes becomes necessary to determine what organic acids are present in combination. The best method of carrying out such an investigation lies in the use of the Duclaux distillation scheme. A dilute aqueous solution of the free organic acids is distilled under definite conditions. As was shown by Duclaux, each volatile fatty acid distils from an aqueous solution at a definite rate, regardless of the presence of other similar acids, and in this way it is possible to determine what organic acids are present. The method is of value only in the hands of an analyst thoroughly experienced in the technic of the procedure.

Some Effects of Ultra-Violet Light on Paint Vehicles[1]

By George F. A. Stutz

THE NEW JERSEY ZINC CO., PALMERTON, PA.

THE effectiveness of blue and ultra-violet light in accelerating the drying of an oil film is generally recognized.[2] The effect of such light in accelerating the destruction of the film is also well established.[3] The present paper reports some results obtained in an investigation of the mechanism of this accelerating action displayed by ultra-violet light. It seems probable that the decomposition, or "weathering," of an oil film is simply a continuation of the drying of the film, and hence the same reaction or series of reactions must be involved in both.

Method

The effect of ultra-violet light on a mass of wet oil has been studied by placing about 300 cc. of oil in a 400-cc. flask of

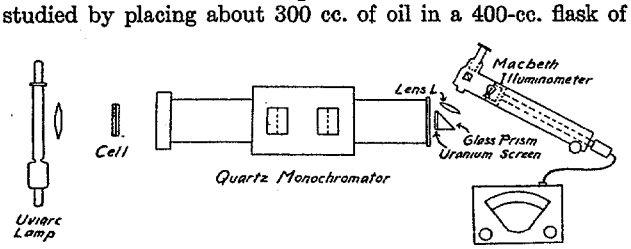


Figure 1—Apparatus for Determining Light Absorption by Oil

clear fused quartz, and exposing it to a Cooper-Hewitt quartz Uviarc at a distance of 30 cm. (12 inches). The oil was stirred continuously with a small glass stirrer, and a slow stream of air, oxygen, or nitrogen bubbled into the oil. The temperature stayed nearly constant, at about 50° C. The oil was sampled at intervals until it had attained a considerable body. The viscosity of the several samples was determined by use of the Gardner-Holt tubes and, in the case of the samples beyond the range of the tubes, the result was obtained by timing the rise of the air bubble in the tube and assuming the rate of rise to be inversely proportional to the viscosity.[4]

The molecular weights were very kindly determined by J. S. Long, of Lehigh University, using the freezing point method.[5]

As a further means of studying the action of ultra-violet light and the changes it accelerates, the degree to which such light is absorbed by the oil was measured. This absorption was determined in the wave-length interval from 3655 Å. to 2300 Å., using an ultra-violet spectrophotometer. A diagram of the apparatus, as used, is shown in Figure 1. Light from the quartz Uviarc lamp passes through the quartz cell containing a thin film of oil and is dispersed in the Bausch & Lomb quartz monochromator. In order to measure visually the intensity of the ultra-violet light transmitted, A. H. Pfund suggested the use of a thin screen of fluorescent uranium glass cemented to a clear glass prism. The screen is viewed from above at an angle of 60 degrees or more, the lens L rendering parallel the light from the foreshortened image of the slit. When so viewed the fluorescent light is particularly brilliant, and is easily photometered by means of the Macbeth illuminometer. The intensity of the fluorescent light is proportional to the intensity of the radiation falling

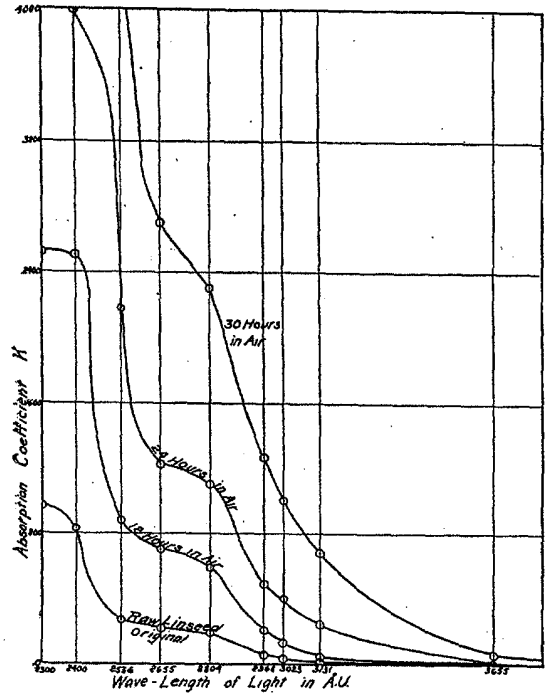
[1] Presented before the Midwest Regional Meeting and the Meeting of the Section of Paint and Varnish Chemistry of the American Chemical Society, Madison, Wis., May 27 to 29, 1926.

[2] Gardner, *Paint Mfrs. Assoc. U. S., Tech. Circ.* **172**.

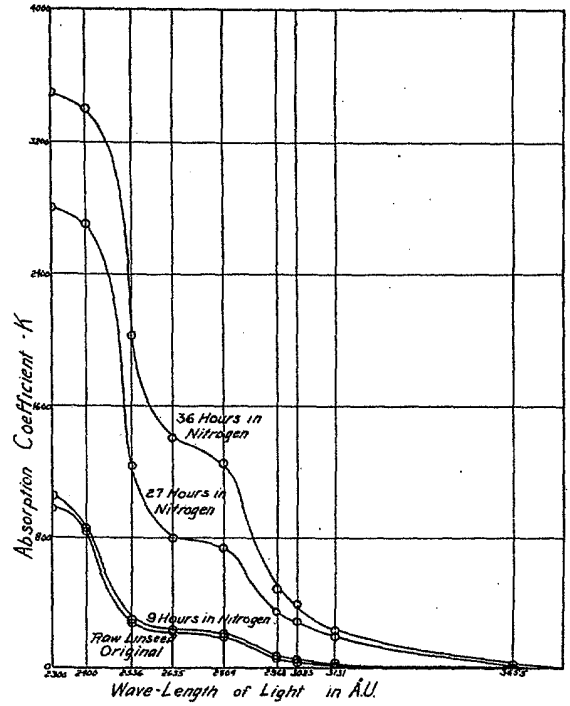
[3] Nelson, *Proc. Am. Soc. Testing Materials*, **22**, Pt II, 485 (1922); Nelson and Schmutz, *Ibid.*, Pt. II, 920 (1924).

[4] Barr, *Phil. Mag.*, **1**, 395 (1926).

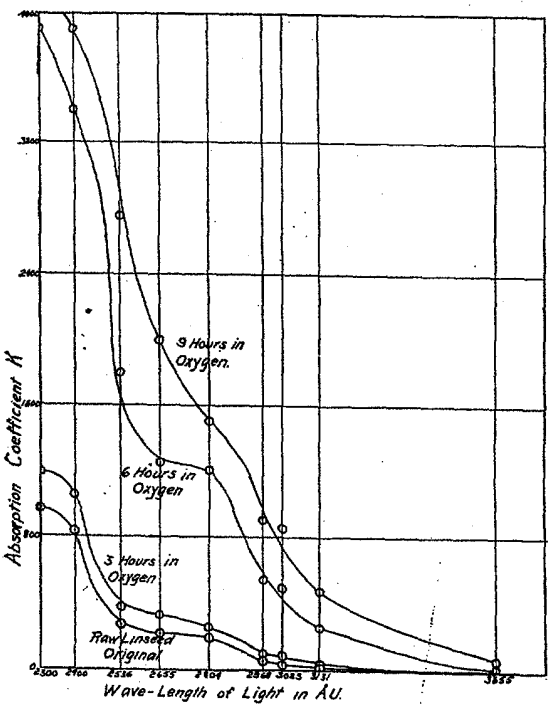
[5] Long and Smull, THIS JOURNAL, **17**, 138 (1925).



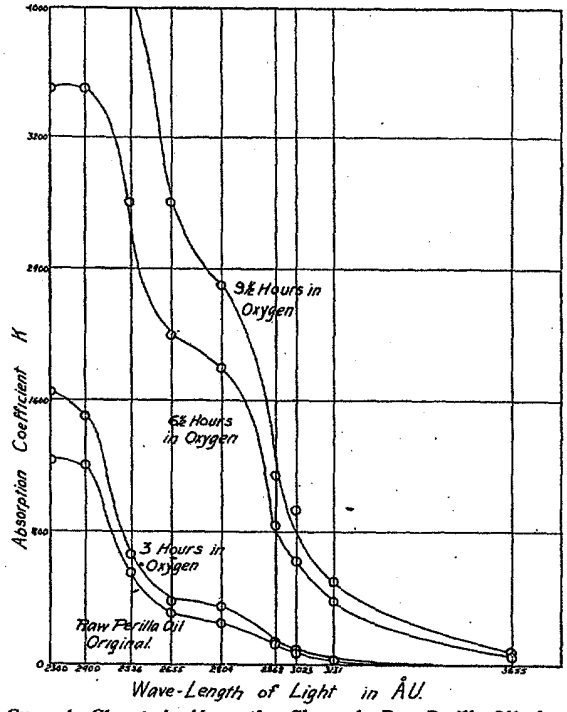
Curve 1—Change in Absorption Shown by Raw Linseed Oil after Exposure to Ultra-Violet Light in the Presence of Air



Curve 3—Change in Absorption Shown by Raw Linseed Oil after Exposure to Ultra-Violet Light in Presence of Nitrogen



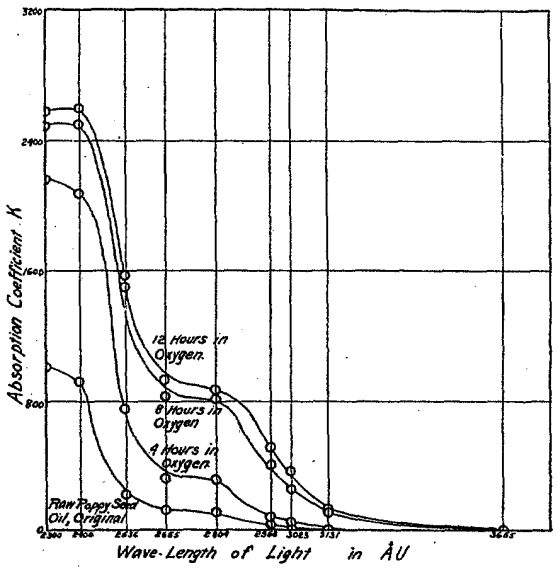
Curve 2—Change in Absorption Shown by Raw Linseed Oil after Exposure to Ultra-Violet Light in Presence of Oxygen



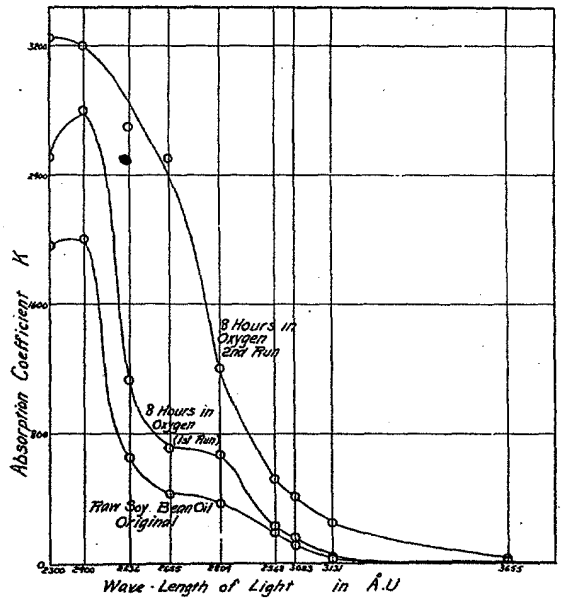
Curve 4—Change in Absorption Shown by Raw Perilla Oil after Exposure to Ultra-Violet Light in Presence of Oxygen

upon the fluorescent screen, and hence a direct measure of the light transmitted by the oil film is obtained. By so viewing the fluorescent screen at an angle, no difficulty is experienced from "impure radiation" in the monochromator, since such "impure radiation" is due chiefly to longer wave lengths, not affecting the fluorescent screen.

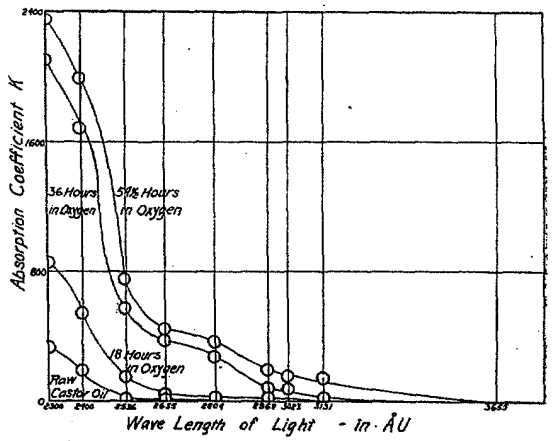
The quartz cell, containing the oil, consists of two quartz plates, separated at one end by a thin strip of tinfoil. The angle of the wedge so formed, and hence the thickness of any portion of it, is found by measuring the set of interference fringes obtained on reflecting monochromatic light from the two surfaces of the wedge. The transmission of several different thicknesses of each oil sample was measured to give check values. The degree of absorption shown by the oil is



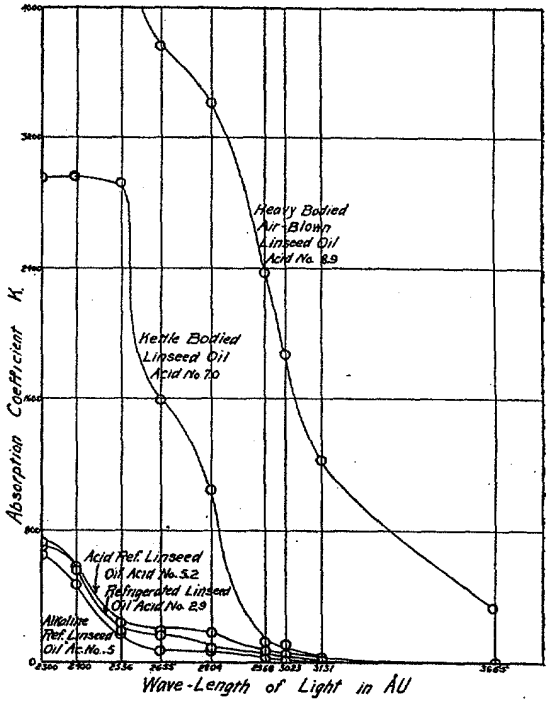
Curve 5—Change in Absorption Shown by Raw Poppy-Seed Oil after Exposure to Ultra-Violet Light in Presence of Oxygen



Curve 6—Change in Absorption Shown by Raw Soy Bean Oil after Exposure to Ultra-Violet Light in Presence of Oxygen



Curve 7—Change in Absorption Shown by Castor Oil after Exposure to Ultra-Violet Light in Presence of Oxygen



Curve 8—Absorption Shown by Several Samples of Commercial Linseed Oil

best expressed in terms of the absorption coefficient K calculated from the relationship

$$I = I_0 10^{-kt}$$

where I = intensity of transmitted light
I_0 = intensity of incident light
t = film thickness in centimeters

Results

The changes in the physical and chemical constants of the oils after exposure to ultra-violet light are recorded in Table I.

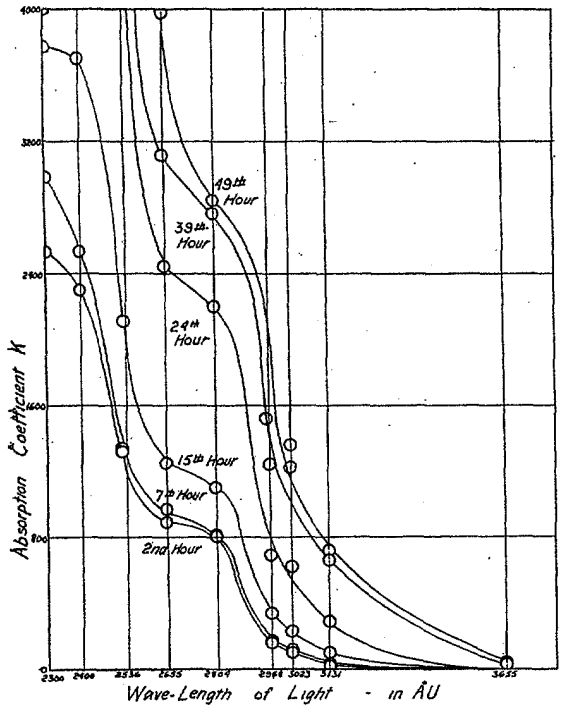
The degree of absorption of ultra-violet light by the several samples before and after exposure is shown in the series of curves, 1 to 7, in which the absorption coefficient K is plotted against the wave length.

The degree of absorption shown by several commercial samples of treated and bodied linseed oils is recorded in Curve 8. Similar results for a series of samples taken at intervals during an air-blow of linseed oil are shown in Curve 9; Curve 10 records the absorption of several oil fatty acids, and of the monoglyceride of linolenic acid.[6]

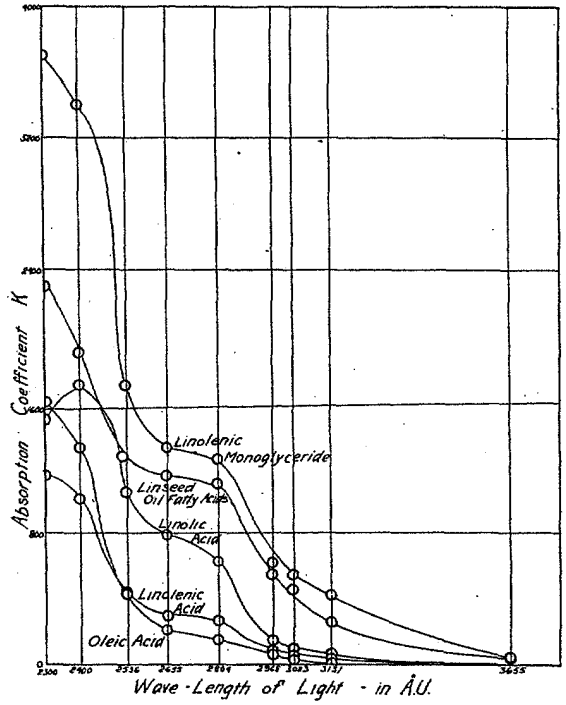
Discussion

Examination of the data in Table I shows that the effect of exposure of wet oils to ultra-violet light is similar to the effect of heat and air-blowing. Increases in viscosity, molecular weight, and refractive index are accompanied by a decrease in the iodine number. The acid number also increases

[6] The writer is indebted to J. S. Long for these samples of acids and for the linolenic monoglyceride.



Curve 9—Absorption Shown by Several Samples of Linseed Oil Taken at Intervals during an Air-Blow (Commercial Scale)



Curve 10—Absorption Shown by Acids Contained in Linseed Oil and Monoglyceride of Linolenic Acid

steadily with increasing exposure to light. It must be remembered that the temperature of the oil remains at about 50° C. and, therefore, very little acid can be volatilized. The light has the additional effect of bleaching the oil until nearly colorless.

The increase in the absorption of ultra-violet light, with increase in molecular weight and body, is of interest. According to Draper's law, only the light absorbed is capable of causing photochemical action. The longer the oil is exposed to light, the more absorbing it becomes, and hence the greater is the effect of the light. The effect is cumulative.

It is noticeable that with increasing molecular weight and body the absorption curve does not change its general shape, but is simply raised. The indication is that the material or materials causing this characteristic absorption of ultra-violet light are present in the original sample, and bodying the oil simply causes an increase in the concentration of such materials. Such increase cannot be due to an increase in acid content, since the pure acids themselves have a less absorption, usually, than the oil samples containing only 4 or 5 per cent of such acids.

This study of the absorption of ultra-violet light by paint vehicles is being extended to dry films.

Acknowledgment

The author wishes to acknowledge the assistance and criticisms of the members of the Research Division of the New Jersey Zinc Company, the help rendered by J. S. Long, and the assistance of C. Hall in making the observations.

Table I—Changes in Physical and Chemical Constants of Oils after Exposure to Ultra-Violet Light

Exposure to U. V. light hours	Gas present	Viscosity poises	Mol. wt.	Refractive index at 26° C.	Iodine No. (Hanus)	Acid No.
		Raw Linseed Oil				
0		0.4	773	1.4751	175	3.4
12	Air	0.75	910	1.4775	171	4.5
24	Air	12.5	1290	1.4779	117	7.4
30	Air	118.0	1785	1.4832	106	8.5
3	Oxygen	0.6	969	1.4753	169	3.7
6	Oxygen	2.25	1551	1.4786	127	7.0
9	Oxygen	22.0	1858	1.4815	113	9.4
9	Nitrogen	0.55	788	1.4750	160	3.5
27	Nitrogen	2.85	—	1.4785	149	5.5
36	Nitrogen	5.25	1220	1.4803	113	5.5
		Perilla Oil				
0		0.50	762	1.4773	181	11.0
3	Oxygen	0.65	844	1.4780	154	11.5
6.5	Oxygen	5.25	1364	1.4839	143	14.7
9.5	Oxygen	33.0	1930	1.4851	116	15.0
		Poppy-Seed Oil				
0		0.55		1.4692	123	5.5
4	Oxygen	1.1		1.4711	123	5.9
8	Oxygen	4.60		1.4747	105	11.6
12	Oxygen	5.25		1.4750	87	12.4
		Soy Bean Oil				
0		1.0		1.4706	119	8.0
8	Oxygen	2.0		1.4730	114	9.5
8	Oxygen	5.7		1.4750	113	8.5
		Castor Oil				
0		4.95		1.4729	81	1.1
18	Oxygen	5.45		1.4738	70	2.3
36	Oxygen	18.07		1.4749	—	11.6
54.5	Oxygen	47.50		1.4759	70	28.0

Manufacture of Carbon Black on Public Domain—The Department of the Interior has granted to George B. Jenkinson, of Denver, Colo., oil and gas leases, on a royalty basis, on 2560 acres of land in Grand County, Utah, as a result of the discovery of gas adapted for the manufacture of carbon black. It is expected that a carbon black plant will soon be constructed on these leaseholds.

The leases were granted as the result of a discovery of gas peculiarly adapted for the manufacture of carbon black. The leases stipulate that the gas may be used for this purpose, provided modern and improved methods are employed, and further that if, after ten years, the Secretary of the Interior finds a demand for the gas for domestic or industrial purposes, the lessee shall be required to supply the gas to gas-line connections.

The leases also provide that where the gasoline content is more than one-half gallon per 1000 cubic feet, the gasoline shall be extracted and a royalty paid to the Government on all gasoline produced.