

Honig and Singleterry (3) have concluded that sodium phenyl stearate in benzene is organized into three types of structure: a) long polymeric chains of anhydrous soap held together by ionic forces; b) a small, compact micelle which exists in the presence of a fraction of a mole of various polar additives per mole of soap; and c) an extensive but loosely bonded structure formed through a bridging between small micelles by an excess of certain polar additives. Extended structures of Types 1 and 3 postulated by these authors could explain some of the larger aggregates present in detergent oils. Much further work remains to be done however before a complete explanation of these structures can be given.

### Summary

Ultracentrifugation and viscosity data indicate that the sulfonate type of detergents normally exists in hydrocarbon solvents as small micelles approximately two molecular lengths in diameter, ranging in shape from nearly spherical to rodlike. The micellar size is shown, in the case of calcium petroleum sulfonate, to change with concentration and temperature. Analysis of the sedimentation patterns shows that, while

Aerosol O.T. appears essentially monodisperse, calcium petroleum sulfonate shows a marked distribution of micellar weights. Ultracentrifugation and electron microscopy show that larger aggregates sometimes exist in solution together with small micelles. These aggregates may result from association of various polar compounds with the detergent micelles.

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## Bleaching of Drying Oils by Ionizing Radiation

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EXPOSURE OF DRYING OILS to ionizing radiation changes a number of properties. These include color, drying characteristics, iodine number, molecular weight, refractive index, viscosity, and hexabromide number, alkali resistance and gas proofness of varnishes from the oils (1, 2). One of the most striking of these changes is bleaching of the oil. This effect was mentioned as early as 1927 when linseed and perilla oils were made almost water-white by electrons from a cathode ray tube (1). Bleaching was again reported in 1956 after the development of nuclear reactors and electron accelerators stimulated a study of the effects of ionizing radiation on tung oil. After exposing the oil to neutrons, *gamma* radiation, or electrons, a color decrease was noted and described briefly (2).

The destruction by ionizing radiation of carotenoids, one of several pigment classes found in drying oils (3), was previously reported in several other systems. The carotenoids were studied in connection with the retention in irradiated foods of the biological activity of  $\beta$ -carotene and vitamin A. *Beta* and *gamma* radiation destroyed the carotenes in butter (4, 5) and dehydrated butter fat (6). Mackinney found that bleaching of the carotenoids in carrot root oil required more *gamma* radiation than those in corn oil (7). Pure  $\beta$ -carotene (6-8) and lycopene (7) in hexane were destroyed with small amounts of ionizing radiation. Lycopene in methyl oleate or methyl linoleate was destroyed by nearly the same dose as in hexane. In contrast, methyl stearate solutions of lycopene were slowly bleached under similar conditions (7). Selected drying oils were therefore irradiated, and their degree of bleaching was compared with those above. The radiation requirements, the effect of environment, and the mechanism of bleaching were emphasized.

### Experimental

The oils used were commercial products. Nonbreak safflower and soybean oil and nonbreak bleached linseed oil were obtained from the Pacific Vegetable Oil Corporation. The tall oil fatty acids were purchased as Unitol ACD from the Union Bag-Camp Paper Corporation. The oleic acid was USP special, light quality.

Three sources of ionizing radiation were used. *Gamma* radiation was obtained from cobalt-60 at a rate of  $3.1 \times 10^5$  reps<sup>1</sup>/hour (9). A "traveling wave" linear accelerator (10) provided 6 Mev electrons at a dose rate of 3 Megareps/minute. Electrons from a 2-Mev Van de Graaff accelerator (11) were also used, especially for large-scale runs.

Most irradiations were done with 6 Mev electrons and a sample thickness less than the penetration of the beam (1.3 in.). This provided a constant radiation level throughout the sample. The oil was contained in a beaker equipped with a side arm just above and at a 45° angle to the liquid level to allow introduction of helium. The oil was maintained at room temperature by immersion of the beaker in circulating cold water or by giving the radiation in increments. Large portions of oil were stirred with a magnetic stirrer and bleached, using 2 Mev electrons from the Van de Graaff. Samples exposed to the cobalt source were sealed in glass ampoules with a small air space.

The total radiation (dose) was determined by the exposure time at a constant radiation level (dose rate). The dose was measured by its known relationship to the color change in an irradiated chip of cobalt glass (12). The dose rate was constant during an

<sup>1</sup> A rep (roentgen equivalent physical) corresponds to an energy absorption of 93 ergs/g. of sample and a Megarep to  $93 \times 10^6$  ergs/g.

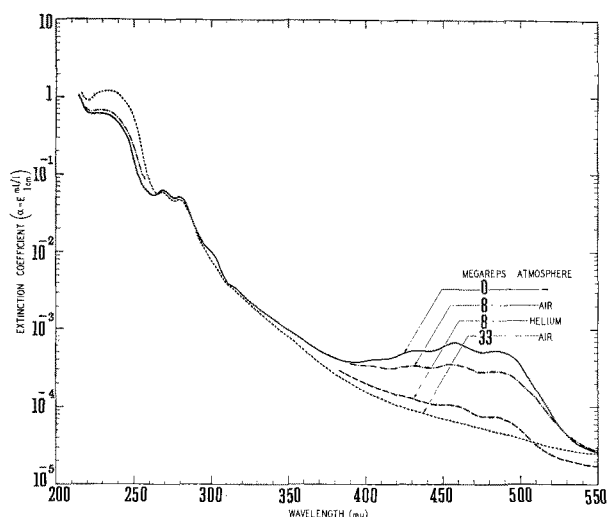


FIG. 1. Absorption spectra of irradiated safflower oil.

experiment so that the cumulative dose was directly proportional to the cumulative time.

The reaction was followed by removal of aliquots for measurement of the visible and ultraviolet spectra in iso-octane. Examples are shown in Figure 1. A Cary recording spectrophotometer Model 14 was used. The infrared spectra were taken in iso-octane, using a Perkin-Elmer Model 21 infrared recording spectrophotometer. The Gardner color was determined by comparison with Gardner 1933 color standards.

### Results and Discussion

**Radiation Requirement.** When safflower oil was bleached by 6 Mev electrons, the logarithm of the percentage of the original absorption at 455  $m\mu$  was proportional to the dose, as shown in Figure 2. The absorption at this wavelength was directly proportional to the Gardner color. Percentage of bleaching was plotted against dose better to depict the radiation required for a given degree of bleaching. To compare rates it was usually more convenient to plot the logarithm of the optical density *versus* dose. This linear relationship was also found when published data (7, 8) were plotted logarithmically. From these

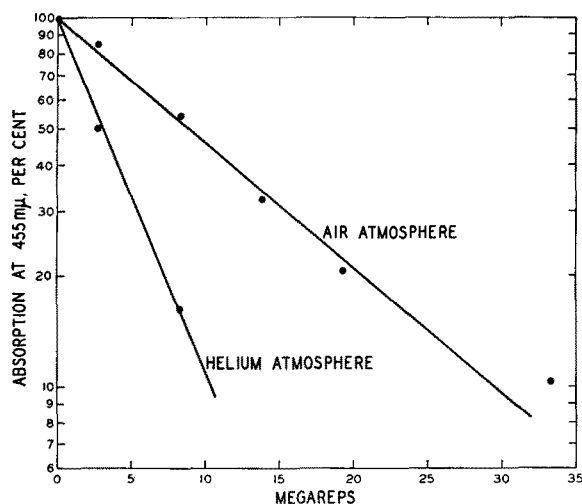


FIG. 2. Bleaching of safflower oil by ionizing radiation.

TABLE I  
Radiation Required for Bleaching

Material	Radiation	Initial optical density <sup>a</sup>	$\lambda$ , $m\mu$	Megareps required for a percentage bleaching		
				10%	63%	90%
Safflower oil-air	Electrons	0.64	455	1.3	12.5	29.5
helium	Electrons	0.64	455	0.5	4.5	10.4
Tall oil fatty acids-helium	Electrons	0.08	455 <sup>b</sup>	2.2	....	....
Linseed oil-air <sup>c</sup>	$\gamma$ -	0.20	310 <sup>*</sup>	5.2	....	....
Soybean oil-air <sup>c</sup>	$\gamma$ -	0.97	455	0.3	3.2	7.8
Safflower oil-air <sup>c</sup>	$\gamma$ -	11.5	446	0.4	3.6	8.4
Carrot oil-air <sup>d</sup>	$\gamma$ -	0.39	450	0.85	....	....
Corn oil-nitrogen <sup>d</sup>	$\gamma$ -	0.11	....	0.16	....	....
$\beta$ -Carotene in hexane <sup>e</sup>	Electrons	ca 25	420	0.08	0.78	1.76
$\beta$ -Carotene in hexane <sup>d</sup>	Electrons	ca 8.6	420	0.06	0.58	1.30
Lycopene <sup>d</sup> in hexane	$\gamma$ -	8.62	452	0.015	0.12	0.28
hexane <sup>d</sup>	$\gamma$ -	1.72	452	0.013	0.10	0.27
methyl stearate	$\gamma$ -	13.8	503	0.006	0.07	0.16
methyl oleate	$\gamma$ -	0.75	500	0.17	....	....
methyl linoleate	$\gamma$ -	0.75	500	< 0.01	0.06	0.15
	$\gamma$ -	0.75	500	< 0.01	0.07	0.16

<sup>a</sup> Oil concentration, 100%. <sup>b</sup> No peak. <sup>c</sup> Limited, in sealed tube. <sup>d</sup> Reference (7). <sup>e</sup> Reference (11). \* Shoulder.

plots the radiation required for given percentages of bleaching in various systems was determined as listed in Table I. The dose required for safflower oil in air was close to that for carrot oil and tenfold greater than for lycopene in methyl stearate. Soybean oil was bleached by a dose comparable to that for safflower oil. Linseed oil and tall oil fatty acids were bleached more slowly.

If a large amount of oil were bleached so that all of the electrons were absorbed, then the logarithm of the color was still proportional to the dose. Thus, at a constant dose rate, the time to a given color for a large-scale bleach operation could be predicted, once the initial rate was found.

The degree of bleaching for a given dose was dependent on the radiation source. *Gamma* radiation from cobalt-60 was somewhat more efficient. This was attributed to the dose rate, which was 0.2% of that from the accelerator. The cumulative effect of *gamma* radiation on various oils in the presence of only a small amount of oxygen is shown in Table II.

**Spectra.** Maxima at various wavelengths in the visible spectrum could be used to follow the bleaching. For example, in safflower oil the changes at 431-2  $m\mu$  and 483-4  $m\mu$  were proportionally the same as at 455-6  $m\mu$ , the major peak. For the tall oil fatty acids there was no peak at a longer wavelength than 310  $m\mu$ . The logarithm of the optical density at that wavelength was however proportional to the dose.

In addition to the destruction of materials absorbing in the visible region of the spectrum, ionizing radiation affected groups absorbing in the ultraviolet, as shown in Table III. The greatest change in addition to bleaching was the increase in absorption at 233-4  $m\mu$  because of diene conjugation. The optical density at this wavelength for soybean and safflower oils increased regardless of the atmosphere and was actually greater in helium. In contrast, there was no change in diene content when the tall oil fatty acids were bleached. Triene conjugation in the oils at 268-9  $m\mu$  increased slowly with the dose but then

TABLE II  
Bleaching of Drying Oils by *Gamma* Radiation <sup>a</sup>

Oil	Linseed	Safflower	Soybean	Oleic acid
Gardner color				
Before.....	5+	8	10+	3+
After.....	5	4	6	2

<sup>a</sup> 5 Mreps.

TABLE III  
 Spectral Changes in Safflower Oil Irradiated <sup>a</sup> in Air

Cumulative dose, Mreps.....	0	2.6	7.9	13.2	18.9	33.3
Gardner color.....	7	6+	5	3+	3	1
Optical density <sup>c</sup> at						
483-4 m $\mu$ .....	0.530	0.446	0.282	0.165	0.100	0.048 <sup>b</sup>
455-6 m $\mu$ .....	0.636	0.541	0.345	0.205	0.133 <sup>s</sup>	0.066 <sup>b</sup>
431-2 m $\mu$ .....	0.546	0.496	0.330	0.212	0.148 <sup>s</sup>	..... <sup>b</sup>
405 m $\mu$ .....	0.452 <sup>s</sup>	0.432 <sup>s</sup>	0.326 <sup>s</sup>	..... <sup>b</sup>	..... <sup>b</sup>	..... <sup>b</sup>
317 m $\mu$ .....	3.4 <sup>s</sup>	3.4 <sup>s</sup>	3.4 <sup>s</sup>	..... <sup>b</sup>	..... <sup>b</sup>	..... <sup>b</sup>
278-9 m $\mu$ .....	51.2	61.9	67.4	45.0	48.6	46.0
268-9 m $\mu$ .....	62.3	75.3	82.8	55.1	59.8	57.5
233-4 m $\mu$ .....	568 <sup>s</sup>	597 <sup>s</sup>	642 <sup>s</sup>	791	845	1202
228 m $\mu$ .....	580	636	669	..... <sup>b</sup>	..... <sup>b</sup>	..... <sup>b</sup>

<sup>a</sup> 6 Mev electrons. <sup>b</sup> No peak. <sup>c</sup> Oil concentration, 100%. <sup>s</sup> Shoulder.

dropped to close to its initial level and remained constant. Similarly, with  $\beta$ -carotene in hexane, the optical density at 275 m $\mu$  and 340 m $\mu$  increased and then dropped on continued irradiation (7). A similar observation with lycopene at 363 m $\mu$  was described (7). Tetraene absorption at 317 m $\mu$  was slight, and no significant changes were observed. A sample of soybean oil with an absorption maxima at 668 m $\mu$  caused by pheophytin (3), a chlorophyll derivative, was bleached successfully. This indicates a potential use of radiation for bleaching of green oils. There was no change in the infrared spectrum of the various oils.

**Oxygen Effect.** The inhibiting effect of oxygen on radiation decolorization was pronounced. The enhanced rate in helium is shown in Figure 2 while the change in spectra with a given dose in air compared to helium is shown in Figure 1. Mackinney noted that destruction of  $\beta$ -carotene in carrot root and corn oils decreased by irradiation in the air (7). Chalmers *et al.* (6) did not report any enhancement of rate on radiation bleaching of butter in nitrogen. Oxygen inhibition of ionizing radiation bleaching is opposite to the effect of oxygen on bleaching by ultraviolet radiation. In the presence of ultraviolet no bleaching of vegetable oils (13) or butter (14, 15) occurred in an inert atmosphere. Ionizing and ultraviolet radiation thus brought about the same effect by different mechanisms.

**Cost.** The exact relationship between the degree of bleaching and the dose allowed the cost of a given amount of bleaching to be estimated easily. For safflower oil in helium about 12 Megareps were required to bleach from a Gardner color of 7 to 1. At present electron accelerators are the cheapest source of ionizing radiation at \$2 to \$4.50 per kilowatt (16). For an average cost of \$3 per kilowatt and 100% utilization of the radiation in batch runs as previously described, safflower oil in an inert atmosphere could be bleached for 4.2¢ per pound. Ionizing radiation may be one-third or less the present cost in the future if improved electron accelerators are built (10). Radiation bleaching would then cost in the order of 1¢ per pound.

**Mechanism.** Radiation bleaching of drying oils could be the result of hydrogenation of the conjugated double bonds responsible for the color of the pigments. The first step in the hydrogenation could be the addition of atomic hydrogen to a double bond to form a radical. This could then abstract a hydrogen atom from the solvent with hydrogenation of the double bond as the result. Support for this hypothesis, especially for carotenoid pigments, came from the irradiation of  $\beta$ -carotene in hexane. When the degradation products were separated, material with

fewer conjugated bonds and absorbing at lower wavelengths was found (7). This could have been formed by hydrogenation of the double bonds, especially those toward the center of the conjugated system. The formation of stearic acid from oleic acid on irradiation (17) also demonstrated that double bonds could be hydrogenated. A recent example (18) of hydrogenation of lower olefins was the use of ethylene and propylene as scavengers for hydrogen atoms in the radiolysis of hydrocarbons.

Hydrogen atoms involved in bleaching originate from the reactions of ionizing radiation with the solvent. These reactions may be the formation of olefins (19, 20) and polymerization (21), as previously reported for hydrocarbons and esters. Both can involve as the first step the cleavage by radiation of a carbon-hydrogen bond to give a hydrogen atom<sup>2</sup> and an organic radical. The latter can then dimerize, disproportionate, or lose another hydrogen atom to form olefin. When olefins were initially present, as in the drying oils, loss of hydrogen atoms from the two adjacent methylene groups next to a double bond would produce diene conjugation. The observed increase in diene absorption at 233-4 m $\mu$  (Table III) supports this hypothesis. As the number of conjugated double bonds in a molecule increased, further dehydrogenation would have to compete with hydrogenation. This would explain the fluctuation observed in triene concentration. A decrease in triene and increase in diene absorption reported by Lang and Proctor (23) for irradiation of edible oils could be explained by the same mechanism as bleaching.

The hydrogen for bleaching of the pigments in tall oil fatty acids probably came from decarboxylation of the acids rather than dehydrogenation as no increase in conjugated diene was observed. This lack of diene formation may result from an ability of the carboxylic acids selectively to use radiation energy for decarboxylation rather than dehydrogenation. The former was reported as the principal reaction on irradiation of fatty acids (24). Most of the hydrogen atoms produced on decarboxylation are used to form the hydrocarbon from the acid and are therefore not available for bleaching. This could explain the lower percentage of bleaching of the pigments in tall oil fatty acids.

The protective action of oxygen fits in well with the hypothesis that dehydrogenation is the main source of hydrogen for bleaching. The known (25) suppression of dehydrogenation of hydrocarbons by oxygen agrees with our observation that dehydro-

<sup>2</sup> Under the influence of ionizing radiation, hydrocarbons may lose molecular hydrogen (22). This may contribute to olefin formation and the gas observed during bleaching but would not affect the mechanism of the latter. It may help explain the large increase in conjugated diene accompanying the bleaching of a small amount of pigment.

genation to conjugated diene was greater in helium than in air. In a related system (7)  $\beta$ -carotene destruction was less in oils exposed to air rather than nitrogen. This indicated a greater sensitivity to reactive intermediates, such as hydrogen atoms, than to peroxides and carbonyls, which form on irradiation in air (26).

### Summary

- (1) Changes in the absorption spectra of drying oils, especially safflower, on exposure to ionizing radiation were followed.
- (2) Bleaching of the oil was plotted as a linear function of the logarithm of the absorption in the visible spectrum *versus* the dose.
- (3) Oxygen inhibited radiation bleaching.
- (4) The cost of bleaching safflower and similar oils by electrons was estimated to be about 4 cents/pound.
- (5) The mechanism of radiation bleaching was postulated to involve hydrogenation of the pigments by hydrogen atoms. These were obtained by dehydrogenation of the oils or by decarboxylation of fatty acids.

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## The Determination of the Unsaponifiable Matter of Tall Oil Distillates

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TALL OIL, a relatively new source of rosin and fatty acids, is derived from Southern Pine as a by-product of the kraft paper industry. Distillation of crude tall oil produces fractions which are predominately either rosin acids or fatty acids. Fatty acids of 98-99% purity are readily attainable. Impurities associated with these fatty acid fractions are rosin acids and unsaponifiable matter.

Present advances in the preparation of tall oil fatty acids are concerned with control of uniformity through chemical composition. Producers of tall oil products have therefore devoted considerable research time to perfection of analytical methods for the determination of the fatty acid, rosin acid, and unsaponifiable content of the various fractions. While procedures (2) for the determination of fatty acids and rosin acids give accurate and reproducible results, considerable controversy has arisen over determination of the unsaponifiable content of tall oil fractions.

At present two official methods are used for determining the unsaponifiable content of oils, fats, and wax products. Both require complete saponification of the sample followed by extraction of the soap solution with a suitable nonaqueous solvent. The A.S.T.M. (2) procedure specifies the use of diethyl ether as the extractant. Separatory funnels are used to separate the aqueous and nonaqueous phases. The A.O.C.S. (1) procedure recommends petroleum ether as the solvent with cylinders and glass siphons for the removal of the nonaqueous layer. A total of seven 50-ml. washes is used to remove all the water-insoluble components of the saponification mixture. The basic difference between these two methods lies in the type

of solvent used for the extraction of the unsaponifiable matter.

Freyer and Weston (3) state that "the most suitable solvent to employ is probably petroleum ether fractionated to distill at 40°C. This dissolves much less soap than does methylated ether. The latter however is always safer as it dissolves a wider range of products insoluble in water." Report of the subcommittee on determination of unsaponifiable matter in oils and fats and the unsaponified fat in soaps to the standing committee on Uniformity of Analytical Methods (5) states that "there is a considerable amount of evidence that the extraction of unsaponifiable matter by means of petroleum spirit is incomplete, especially from certain fish oils."

Included in a later report on unsaponifiable matter (4) is the statement, "Attempts to use ethyl ether with the continuous and F.A.C. methods were generally unsatisfactory due to the formation of emulsions." The report also contained a comparison of per cent unsaponifiables as determined by a variety of methods using ethyl ether or petroleum ether. Results were within reasonable agreement regardless of method or solvent used.

### Experimental

This paper presents data obtained in the comparison of A.O.C.S. and A.S.T.M. methods, using diethyl ether or petroleum ether for the determination of unsaponifiables in tall oil distillates. Attempts were also made to learn what factors and impurities contributed to the formation of unsaponifiable matter during processing of tall oil, fatty acid fractions.