contribution to the light scattering intensity of critical opalescence. At the lower temp the system is close to the critical point.

Conventional heats of micellization were calculated from Equation [2] for solutions containing 0–0.06*M* NaCl. These results show in Table I.

Conclusion

Hyamine-1622 NaCl solutions at zero and low NaCl concn have low CMC values which are close to those observed in non-ionic detergent systems. Flockhart (17) has shown, in comparative studies of soaps of different hydrocarbon chain lengths, that the lower the CMC the more negative will be the heat of micellization.

The low CMC values and the large negative values of the heats of micellization of the long chain quaternary ammonium salts, which form coacervates, suggest that these micellar systems show some of the properties of simpler monomeric quaternary ammonium salts. The major property of interest in this respect is the hydrophobic character of the quaternary ammonium cation. Hyamine-1622 NaCl micellar solutions exhibit a high degree of sensitivity to small changes in NaCl concn (16) and temp. In addition, these systems show a marked electrolyte specificity (18). These are properties observed in hydrophobic colloidal systems.

In an opposite sense, Matijević and Pethica (14) explain the small negative values of ΔH_m for sodium dodecyl sulfate in terms of the large positive contribution to ΔH_m due to the desolvation of the highly solvated anion of this salt. Both the Matijević and Pethica study and Hyamine-1622-NaCl study indicate that the solvation properties of micellar systems play a significant role in the energetics of micelle formation.

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Catalysts for Selective Hydrogenation of Soybean Oil[1]

III. Hydrogenation Catalysts Prepared on Molecular Sieves and Other Supports

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Abstract

A survey of nickel, platinum and palladium catalysts prepared on silicas, aluminas and molecular sieves indicated that the nature of such supports contributed importantly to selective hydrogenation of soybean oil. Nickel-molecular sieve catalysts provided both high hydrogenation selectivity and low *trans*-isomer formation. Some kind of spatial hindrance may be postulated in explanation of the results.

Introduction

PRIOR PAPERS in this series were concerned with the development of an experimental evaluation for determining hydrogenation selectivity (1) and application of this method to a variety of commercial catalysts (2). In a kinetic study, Bailey (3) had indicated that under conditions producing selective hydrogenation of soybean oil, the ratio of linolenic to linoleic components reacted was 100/50. With linseed oil, a condition producing a k_{Ln}/k_{Lo} ratio of 2.5 was obtained under selective conditions whereas 1.7 was found under non-selective conditions. This orientation is of particular value in reviewing the survey on selective hydrogenation of soybean oil with various commercial catalysts (2), where the selectivity index ($S_L = k_{Ln}/k_{Lo}$) was 2.4 or better for several platinum, palladium and rhodium catalysts but where many nickel preparations did not demonstrate an S_L value of 2.0. It was felt that development of nickel catalysts would have the greatest import both from a practical as well as technical viewpoint.

The preparation and properties of catalysts for glyceride oil hydrogenation has been reviewed by Feuge (4). While variations in selectivity between different types of nickel catalysts preparations are known, factors producing such selectivity are not presently recognized. Further, it is indicated that platinum and palladium, although producing the most active catalysts, are not selective.

Catalyst Preparation

Impregnation. Most of the catalysts were prepared by impregnation on various supports. The procedure comprised admixture of the support with a metal salt dissolved in sufficient distilled water to form a paste. This mixture was heated with stirring at low heat to drive off excess water and to form a uniform product which was then dried at 110C. This material was placed in a cold muffle and brought slowly to a max temp of ca. 500C. In several cases, the synthetic zeolites were first exchanged with nickel cation, and then impregnated as indicated in Table I. Before

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[1] Presented at the AOCS Meeting, Toronto, 1962.

TABLE I

Impregnated Catalyst Preparations

Carrier		Metal		
Source	g	Salt	g	Atom-layers (nominal)
Davison, silica gel, RD	5.0	$Ni(NO_3)_2 \cdot 6H_2O$	45.5	1.0
	5.0		4.6	0.1
	5.0		2.3	0.05
Davison, silica gel, ID	5.0	$Ni(NO_3)_2 \cdot 6H_2O$	18.5	1.0
	5.0		4.6	0.1
	5.0		2.3	0.05
Cabosil disperse silica	10.0	$Ni(COOH)_2 \cdot 2H_2O$	13.6	1.0
	10.0		2.72	0.2
	10.0		1.36	0.1
Davison Syloid-244	10.0	$Ni(NO_3)_2 \cdot 6H_2O$	32.0	1.0
	10.0		6.4	0.2
	10.0		3.2	0.1
Davison *eta*-alumina	15.0	$Ni(NO_3)_2 \cdot 6H_2O$	36.8	1.0
	15.0		7.4	0.2
	15.0		3.7	0.1
Baymal alumina	28.3	$Ni(NO_3)_2 \cdot 6H_2O$	58.8	1.0
	28.3		11.8	0.2
	28.3		5.9	0.1
Linde No. 4A	8.0	$Ni(NO_3)_2 \cdot 6H_2O$	64.0	1.0
	5.0	$Ni(COOH)_2 \cdot 2H_2O$	25.5	1.0
	5.0		2.6	0.1
Linde No. 13X	10.0	$Ni(COOH)_2 \cdot 2H_2O$	50.9	1.0
	20.0		20.4	0.2
	20.0		10.2	0.1
Davison Z-14	5.0	$Ni(NO_3)_2 \cdot 6H_2O$	40.0	1.0
	5.0		8.0	0.2
	5.0		4.0	0.1
Linde No. 4A	10.0	$PtCl_4 \cdot 8H_2O$	0.25	....
	5.0		1.0	....
Davison GR-511	4.5	$PtCl_4 \cdot 8H_2O$	0.11	....
	4.5		0.55	....
Davison Z-14	4.1	$PtCl_4 \cdot 8H_2O$	0.50	....
Baymal alumina	28.3	$PtCl_4 \cdot 8H_2O$	2.5	....
Davison GR-511	4.5	$PdCl_2 \cdot 2H_2O$	0.075	....
	4.2		0.35	....
Davison Z-14	4.5	$PdCl_2 \cdot 2H_2O$	0.37	....
Linde No. 4A (Ni-exchanged)	5.0	$Ni(COOH)_2 \cdot 2H_2O$	2.0	0.2
Linde No. 13X (Ni-exchanged)	5.0	$Ni(NO_3)_2 \cdot 6H_2O$	40.0	1.0
	5.0		8.0	0.2
	5.0		4.0	0.1

use, each material was reduced at the lowest possible temp for relatively complete reduction, normally in the range 450–550C.

In order to unify the results, coverage of surface was estimated on the assumption that the effective radium of the nickel atom (1.2 Å) described its cross-sectional area. The nominal coverage of the surface shows in Table I.

Exchange. The synthetic zeolites (molecular sieve or Microtrap) were exchanged with nickel cation by allowing 200 ml 2N nickel nitrate solution to stand in contact overnight with 25 g zeolite. After decanting the supernatent liquid, the process was repeated 15 times. Finally, the exchanged material was washed with distilled water until the wash liquid contained no green color. The product was dried overnight at 110C. Before use, the material was reduced, normally in the range 500–550C.

In a number of tests, the exchanged nickel catalysts were impregnated with additional quantities of nickel salt. The drying and reduction steps were as above.

Carriers. A number of catalyst carrier materials was used, as shown in Table II. Pertinent properties are also given.

Supported Nickel Catalysts

Silica in the form of diatomaceous earth is used in industrial preparations because it serves the double purpose of providing an extended surface and acting as a filter aid. Synthetic forms of silica were used to evaluate the influence of surface nature and pore structure, which can be expected to have an influence on hydrogenating selectivity. The impregnation procedure utilized in preparing the catalysts of Table III minimizes $NiO-SiO_2-H_2O$ interactions which can occur with siliceous supports (5,6).

TABLE II

Carrier Materials

Designation	Source	Remarks
RD silica gel	Davison Chemical, Division of W. R. Grace and Co., Baltimore, Md.	Surface area, 850 m^2/g Pore diam (avg), 22 Å
ID silica gel		Surface area, 350 m^2/g Pore diam (avg), 130 Å
Syloid-224		Aerosol, surface area, 300 m^2/g Particle diam (avg), 3.3 μ
eta-Alumina		95% *eta*-form Surface area, 230 m^2/g
Microtrap		
GR-511		Na-form, 4 Å pore diam
Z-14		Na-form, 12 Å pore diam
Cabosil silica	Cabot Corp., Boston, Mass.	Surface area, 200 m^2/g Particle diam range, 150–200 Å Ignition loss at 1000C, <1%
Baymal alumina	Du Pont, Wilmington, Del.	Boehmite (AlOOH), 83.1% HAc, 9.8%; H_2O, 5.0% Surface area, 274 m^2/g Pore diam (avg), 77 Å
Molecular sieve No. 4A	Linde Co., Div. Union Carbide Corp., Tonawanda, N. Y.	Synthetic Zeolite Type A, $Na_2O \cdot Al_2O_3 \cdot 2\ SiO_2 \cdot xH_2O$ Surface area, 750 m^2/g Pore diam, 4 Å
No. 13X		Type X, $Na_2O \cdot Al_2O_3 \cdot 2.5\ SiO_2 \cdot xH_2O$ Surface area, 750 m^2/g Pore diam, 10–13 Å

Comparison of the RD silica gel with the ID silica gel demonstrates that the large pore opening (130 Å) provided appreciably more selective catalysts than the smaller pore openings (22 Å). Since there is a wide variation in pore dimensions, it is apparent that optimum selectivity based on this factor could not be achieved. It is believed significant that the larger-pore catalysts were appreciably more active than the smaller-pore products.

Two finely divided silicas were also evaluated as nickel catalyst supports. Cabosil by virtue of its mode of manufacture is a non-porous form of silica with a particle size range of 150–200 Å. On the other hand, Syloid 244 is highly porous with a particle size averaging 3.3 μ. In both cases, a high degree of selectivity and reactivity occurred at a nickel surface coverage of 0.2.

In general these results with silica suggest that the intrinsic selectivity of nickel on an inert support gives an S_L value of slightly better than 2. Where the nickel is distributed at a thin surface coverage (e.g., 10–20%), the selectivity and reactivity are normally highest except in the case of the small-pore silica gel. At dense (100%) surface coverage, the carrier substrate has no great influence and apparently the catalytic properties of the nickel may suffer lower reactivity, or lower selectivity, or both. These facts suggest that the nickel surface is not used to its fullest extent. At the lowest coverage of silica surface (5–10%), there may be sufficient reaction of nickel with the reactive silica surfaces to inactivate appreciable portions of the nickel surface as shown by van Eijk and Franzen (5,6).

In the use of alumina as a support, substantially different results were received (Table III). Alumina, in the *eta*-form, or as a dehydration product of colloidal boehmite (Baymal) (7), showed high selectivity and reactivity at 100% coverage of the surface with

TABLE III

Supported Nickel Catalysts

Experiment No.	Carrier	Ni atom layers nominal	Temp C	Rate[a] MM/min	S_o	S_L	Ln removed %	Trans isomers %
Silica supported catalysts								
85	SiO_2 gel (Davison RD)	1.0	150	0.48	2.1	1.5	44	14.7
87		0.1	150	0.44	0.4	0.9	14	4.1
90		0.05	150	0.48	0.3	0.9	12	1.7
86	SiO_2 gel (Davison ID)	1.0	150	1.15	2.7	1.8	48	6.4
88		0.1	150	1.28	33.5	1.7	46	7.5
91		0.05	150	0.74	18.0	1.9	68	12.6
103	Disperse SiO_2 (Cabosil)	1.0	150	1.72	4.6	1.0	28	10.4
104		0.2	150	2.07	20.3	2.1	56	10.6
105		0.1	150	1.57	13.9	1.8	40	9.1
141	Disperse SiO_2 (Syloid 244)	1.0	80	0.26	4.1	1.8	32	4.8
142		0.2	80	0.41	13.3	2.1	41	4.0
143		0.1	80	0.23	3.3	1.5	31	4.8
Alumina-supported catalysts								
138	*eta*-Al_2O_3 (Davison)	1.0	50	0.48	16.6	2.0	37	3.6
139		0.2	50	0.29	21.4	1.6	32	4.3
140		0.1	80	0.28	5.5	1.7	44	5.7
121	Baymal-Al_2O_3 (du Pont)	1.0	39.5	0.13	4.7	2.4	46	4.2
122		0.2	150.0	0.077	39.0	1.7	41	37.5
123		0.1	150.0	0.077	35.3	1.8	56	41.8

[a] MM = Millimoles.

nickel. Thus, alumina may have a relatively powerful influence on the nature of nickel catalysts. At low nickel coverage of the fibrillar Baymal alumina, exceptionally high isomerization was observed. Such isomerization activity may be related to intrinsic acidity character as suggested by Pines et al. (8).

The above brief study demonstrates that although the nature of the nickel support was an important factor, simple dispersion on a surface does not appreciably change the nature of selective hydrogenation and that an additional factor was needed.

Molecular Sieve Catalysts

The availability of so-called molecular sieve products provided a means for developing catalysts with quite uniform pore structures. Certain synthetic crystalline inorganic zeolite salts upon dehydration leave a stable crystalline solid containing mutually connected intracrystalline voids of predetermined size (9,10). Several commercial products were used with the approximate openings indicated in Table IV. These supports permit nickel to be deposited within the structure in at least two ways. First, the nickel can be deposited by impregnation by utilizing the molecular shape of the material to achieve selective catalysis. Second, since the materials have cations accessible to exchange, it becomes possible to incorporate nickel directly into the zeolite lattice. These two possibilities along with an impregnated-exchange permutation were evaluated (Table IV). While the results are not incontrovertible, there is evidence that some selectivity was achieved.

The 10–13 Å supports usually provided selective catalysts. This might indicate that the pore structure imposed a limitation on the access of the substrate molecule to active nickel sites. Under favorable conditions this led to selective hydrogenation. On the other hand, when the selective exchanged catalyst used in Expt. 128 was impregnated with nickel, the selectivity was appreciably decreased (Expts. 129–131).

The 4-Å support exchanged with nickel gave a selective hydrogenation at 80C (Expt. 117). When this exchanged catalyst was impregnated with additional nickel, the selectivity was retained (Expt. 116). Upon raising the temp to 150C, the hydrogenation rate was appreciably increased but the selectivity was lowered. This observation suggests

TABLE IV

Molecular Sieve Catalysts

Experiment No.	Pore diameter angstroms	Ni atom layers nominal	Temp C	Rate[a] MM/min	S_o	S_L	Ln removal %	Trans isomers %
Impregnated catalysts								
95	4	1.0	150	0.22	10.5	2.1	30	6.0
96	4	1.0	150	0.49	9.8	1.4	24	11.5
97	4	1.0	150	1.27	7.4	2.0	36	6.5
144	12	1.0	80	0.18	4.1	1.5	29	2.8
145A	12	0.2	80	0.38	9.5	2.3	25	4.1
146	12	0.1	80	0.47	5.3	1.2	32	5.6
98	13	1.0	150	0.32	19.4	2.9	48	13.8
100	13	0.2	150	2.04	12.0	2.1	46	6.3
99	13	0.1	150	1.89	8.3	1.5	32	7.6
Exchanged catalysts								
117	4	<1	80	0.63	22.2	2.3	40	5.7
114	4	<1	150	1.76	8.9	1.3	30	8.5
128	13	<1	65	0.25	20.1	2.7	58	2.8
Impregnated-exchanged catalysts								
116	4	1.0	80	0.50	24.1	2.9	42	4.0
115	4	1.0	150	1.27	33.0	1.9	36	7.5
129	13	1.0	80	0.30	2.9	1.0	35	3.8
130	13	0.2	80	0.57	5.4	1.2	27	4.2
131	13	0.1	80	0.51	4.4	1.4	31	3.2

[a] MM = Millimoles.

TABLE V

Platinum and Palladium Catalysts

Experiment No.	Carrier	Metal concn wt-%	Temp C	Rate[a] MM/min	S_O	S_L	Ln removal %	Trans isomers %
Platinum catalysts								
120	Molecular sieve, No. 4A	1.0	80	0.087	3.8	2.2	68	2.1
134	Microtrap, GR-511	1.0	80	0.48	8.4	2.2	42	4.5
132A	Microtrap, Z-14	5.0	100	0.048	4.9	2.0	39	5.1
135	Microtrap, GR-511	5.0	150	0.092	5.3	1.6	41	10.8
127	Molecular sieve, No. 4A	4.0	150	0.087	8.5	1.4	31	7.3
125	Baymal Al_2O_3	5.0	150	0.13	5.0	1.2	46	7.7
Palladium catalysts								
136	Microtrap, GR-511	1.0	50	0.38	18.6	2.0	37	4.6
137	Microtrap, GR-511	5.0	50	0.26	10.5	1.8	42	4.5
133	Microtrap, Z-14	5.0	80	0.24	15.8	1.8	36	3.7

[a] MM = Millimoles.

that selectivity is not produced by fast reaction rate but that certain time limitations are required. Such selectivity may be related to a molecular accessibility of the catalytic surface.

It is apparent that more work is needed to evaluate the effect of pore size. In the use of the same two types of molecular sieve as a support for platinum, Rabo et al. (11) found that for hydrocarbon isomerization the small pore catalyst restricted escape of product whereas with the large pore size, the critical size of the catalyst exceeded the critical size of the reaction product (e.g., isohexanes). A selectivity for butene-1 hydrogenation in the presence of isobutene was noted for a platinum, 4-Å molecular sieve catalyst (12).

With nickel, it is necessary to heat the catalyst to a temp sufficient to cause oxide reduction. This temp of nickel reduction and that of molecular sieve collapse are quite comparable. Thus, further evaluation of the pre-reduction of such catalysts is an important aspect contributing to selectivity.

Platinum and Palladium Catalysts

A number of platinum and palladium catalysts were evaluated with the results shown in Table V. Primarily, no appreciable advantage can be seen for these catalysts as compared with comparable conventional catalysts (2). In general, hydrogenation rates were appreciably depressed whereas the selectivities were not significantly higher. Of particular interest is the observation that both selectivity and reaction rate were improved at low metal concentrations. The results suggest that selectivity will be most favorable at quite low metal concn, e.g., 0.5% or lower. Here, it is possible that the limited access of the reacting oil to the catalyst surface will serve a highly useful purpose in permitting only selective hydrogenation without concurrent isomerization. The low isomerizations indicated in Table V is noteworthy.

Lithium-Prepared Catalysts

Nash et al. (13) described the ready solution of platinum in molten lithium under vacuum or in an argon atmosphere. The product upon hydrolysis yielded a colloidal material which served as a hydrogenation catalyst. In the present study, lithium solutions of platinum, palladium and rhodium were prepared in this manner and evaluated as catalysts for the hydrogenation of soybean oil (Table VI). Rhodium appeared to show more selectivity than the other preparations. Attempted preparation of iridium and nickel catalysts by the lithium technique were unsuccessful. In general, these experiments imply that while the method of preparation is unusual, the selectivity appears to be no different than is available by more conventional procedures.

Discussion of Results

Recent work on selective hydrogenation has mainly reinforced the findings of Bailey (3). Selectivity is normally attained by a choice of conditions whereby the concn of hydrogen within the sphere of reaction is kept low, and factors leading to fast reaction rate such as high temp and high catalyst concn, generally provided the requisite selectivity. In the present study with selectivity applying almost exclusively to linolenic components, the need for selective catalysts has become particularly evident. Hydrogenation of soybean oil with molecular sieve catalysts has demonstrated that with nickel dispersed on molecularly sized pores, the selectivity is no longer dependent upon the high rate of hydrogenating linolenic double bonds relative to linoleic double bonds. Rather, low temp and reduced reaction speeds provide better selectivity. This is in accord with a view that the adsorbed linolenic molecule cannot proceed to an undesirable high degree of completeness because of some spatial hindrance effects. Thus, because of this factor or because lower hydrogenation temp are possible, concurrent *cis*-to-*trans* isomerization is also appreciably reduced.

Although nickel can be directly exchanged in the synthetic zeolite structure, this does seem to be a necessary condition. Impregnated nickel-molecular sieve catalysts functioned acceptably. Further, platinum and palladium catalysts, which were not exchanged, demonstrated better selectivity at low metal concn and low temp when supported on molecular sieve carriers. Since the activity of noble metal catalysts is intrinsically high, spatial hindrance might prove of special importance in developing selective catalysts.

The current study requires considerable amplification, but substantial progress has been made on the development of truly selective catalysts based on molecular pore structure.

TABLE VI

Lithium-Prepared Catalysts

Experiment No.	Metal	Metal wt-%	Temp C	Rate[a] MM/min	S_O	S_L	Ln removal %	Trans isomers %
60	Platinum	0.050	80	0.22	0.9	0.7	36	5.9
89	Palladium	0.088	35	0.20	8.1	1.8	44	1.7
92	Rhodium	0.015	35	0.040	1.6	2.2	30	5.9

[a] MM = Millimoles.

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Effects of Ionizing Radiations on Fats. II. Accumulation of Peroxides and Other Chemical Changes[1, 2]

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Abstract

The accumulation of peroxides, carbonyl compounds and reducing substances during irradiation and post-irradiation storage of pure fatty acid methyl esters has been studied.

Irradiation and storage of irradiated methyl myristate under vacuum results in formation of small quantities of these compounds. Irradiation under oxygen gives peroxides and carbonyl compounds in yields indicating that every ionization results in the formation of one molecule of each group, and antioxidants have no effect on the formation of these compounds during irradiation.

Irradiation of methyl linoleate under vacuum results in destruction of pre-formed hydroperoxides. During irradiation in oxygen, approximately one-eighth of the peroxides formed arises from the direct reaction of irradiation-induced free radicals with oxygen, while the rest is formed through a chain mechanism with an average chain length of 7.

Peroxides continue to accumulate in irradiated methyl linoleate stored under oxygen at a rate increasing with initial irradiation dose.

Antioxidants have some effect in retarding the formation of peroxides during irradiation of methyl linoleate and during post-irradiation storage, but the effect is small compared to their antioxygenic activity toward simple autoxidation. The effect varies with the nature of the antioxidant and with irradiation dose. Propyl gallate is much less effective than butylated hydroxyanisole and appears to be easily destroyed during irradiation.

Introduction

THE TREATMENT of fats with high energy radiations results in the formation of free radicals which may participate in a number of reactions in the irradiated medium. When molecular oxygen is available, the free radicals readily react with this substance to form hydroperoxides. Decomposition of these peroxides yields new free radicals and a chain oxidation process identical to that prevailing in autoxidation is initiated.

Most studies on the effects of radiations on lipids have been performed on unsaturated fats and it has been impossible to differentiate between the products formed directly as the result of irradiation and those produced through the usual autoxidative chain process. Furthermore, irradiation produces a number of other chemical changes such as formation of carbonyl compounds, polymers, short-chain acids and hydrocarbons, but the formation of these compounds during irradiation and subsequent storage has not been fully investigated.

The results reported here are part of a broader study initiated to obtain additional information on these problems.

Experimental

Preparation and Irradiation of Samples. Methyl myristate was prepared by esterifying myristic acid (Eastman Chemicals) with methanol in presence of H_2SO_4, followed by the usual extraction, washing and drying procedures. After removal of the solvent under vacuum, the residual ester was nearly colorless, had an iodine value (I.V.) of less than 0.1, and was used without further purification.

Methyl linoleate was prepared by urea fractionation of safflower oil fatty acids (1), methylation of the most unsaturated fraction and vacuum fractional distillation of the methyl esters. The I.V. of the fraction used for these studies was 170.2, and purity was better than 95%.

Samples of methyl myristate or methyl linoleate containing 0.01% propyl gallate (PG), α-tocopherol (αT), butylated hydroxyanisole (BHA) and 0.01% each PG and citric acid (CA) were prepared by adding suitable amt of alcoholic solutions of the antioxidants to the methyl esters and removing the alcohol by evaporation under vacuum. In one experiment, methyl linoleate containing 0.1% propyl gallate was used also.

For irradiation under vacuum, one-ml aliquots of the samples were evacuated and sealed in 15-ml pyrex bulbs. For the experiments in an atmosphere of oxygen, 2 ml portions were sealed under oxygen in 40-ml tubes. All samples were irradiated at Materials Testing Reactor, Arco, Idaho, with doses of approximately 2,5 and 8 x 10^6 rads.

The samples were packed in dry ice during shipment to and from the irradiation facility, and they were usually received at our laboratory 2–4 days after irradiation. Controls were shipped with the samples and, with the exception of irradiation, their handling was identical to that of the irradiated samples.

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[1] For paper I of this series, see Ind. Eng. Chem. *49*, 1713 (1957).

[2] Presented at the AOCS Meeting in Minneapolis, 1963.