TABLE V

Effect of Acid Removal from Oil on the Compressive Strength of Foams

| Blown castor oil in polyol[a] | | Equivalent weight of polyol[b] | | |
|---|---|---|---|---|
| Oil No. | Acid value | 100 | 120 | 140 |
| | | Compressive strength of foam, psi | | |
| 6 | 18 | 53 | 41 | 31 |
| 6 Deacidified[c] | 6 | 46 | 41 | 36 |
| 7 | 21 | 50 | 46 | 35 |
| 7 Deacidified[c] | 4 | 46 | 42 | 33 |

[a] See Table II.

[b] Polyols composed of mixtures of oils and triisopropanolamine.

[c] Blown castor oil (200 g) in 700 ml 6/1 MeOH/tetrahydrofuran was passed through column of about 200 g Dowex 1 x 8 in. $OH^-$ form. Column was rinsed with about 300 ml of 6/1 MeOH/THF. Solvent was removed from combined eluates on rotary evaporator.

oil generally increase with increasing degree of oxidation.

A detailed comparison of the properties of foams prepared from raw castor oil and a highly oxidized castor oil is shown in Table III. At each equivalent weight level, the compressive strength of the blown oil foam is higher than that of the raw oil foam. Also, the difference in strength of the two types of foam increases as the polyol equivalent weight is increased. The blown-oil and raw-oil foams do not differ significantly in the other properties measured. The overall composition of these foams is given in Table IV.

The increased strength of foams prepared from oxidized castor oil may be due to increased hydrogen bonding between urethane groups and the oxygen-containing groups ($>C{=}O$, $-OH$) formed during oxidation, or to increased functionality of the oxidized oils. The possibility that the increased strength of these foams was due to the higher free acid content of the blown oils was investigated. These acids would, on reaction with isocyanates, produce a higher content of urea and amide groups, which are known to reinforce urethane polymers (7). Most of the free acid was removed from two samples of blown castor oil by means of a strongly basic anion exchange resin. Foams were then prepared from these deacidified oils and compared with foams prepared from the original oils (Table V). Use of the deacidified oils did not cause any significant change in foam properties. Therefore, the increased strength of these foams is not due just to the higher free acid content of the blown oils.

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# Copolymerization of Methyl Esters of Unsaturated $C_{18}$ Fatty Acids[1]

**F. R. MAYO and CONSTANCE W. GOULD, Stanford Research Institute, Menlo Park, California**

## Abstract

In order to assay the possibilities of making high polymers from linseed oil, the copolymerizations of styrene with the methyl esters of oleic, linoleic, linolenic, and conjugated linolenic acids were studied at 60–130C and copolymerizations of the last three esters with acrylonitrile were studied at 60C. Appropriate free radical initiators were employed in all cases. The esters without conjugated unsaturation show little tendency to enter a copolymer with styrene, but copolymers containing up to 40% by weight of conjugated linoleate can be obtained. Linoleic, linolenic, and conjugated linoleic esters copolymerize readily with acrylonitrile. Products containing up to 45 mole %, 80 wt %, of the conjugated ester can be made. However, methyl eleostearate, with three conjugated double bonds, inhibits the polymerization of both styrene and acrylonitrile. Quantitative comparisons of the behaviors of the esters are made through the copolymerization equation. The probable performance of these and other vinyl monomers in copolymerization with linseed oil is discussed.

## Introduction

THE WORK reported here is a portion of that carried out under Contract No. 12-14-100-4505 (71) with the USDA, directed toward the utilization of linseed oil in emulsion paints. Since linseed oil is unsuitable for use directly in emulsion, and since it does not give a high polymer by itself (except on drying with oxygen), an ultimate objective was to copolymerize linseed oil with some vinyl monomer to make a high molecular weight copolymer. In order to determine the relative reactivities of the various unsaturated groupings in linseed oil toward polymerizing radicals, the individual methyl esters of $C_{18}$ unsaturated fatty acids were examined in bulk or solution copolymerization with free radical initiators.

Review of the literature brought out the following points. Almost all the copolymerization studies involving unsaturated fatty esters involved styrene. Since the unconjugated fatty acid residues are unreactive in copolymerization with styrene below 100C, higher temperatures were usually employed. Here the free radical copolymerization is complicated by the non-radical or Diels-Alder dimerization of the fatty acid residues, and literature data cannot be interpreted quantitatively. Only one paper was susceptible to quantitative treatment. Harrison and Tolberg (1) studied the copolymerization of styrene with methyl esters of $C_{18}$ fatty acids. Their quantitative results extend the previous semi-quantitative conclusions of Hewitt and Armitage (2).

Harrison and Tolberg separated each copolymer from monomer by a tested procedure, and analyzed separately for carboxymethyl and benzoate groups by infrared. Their results are summarized in Table 1. As they point out, the rates of polymerization

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[1] Presented at the Symposium on Recent Advances in Drying Oil Chemistry, Division of Organic Coatings and Plastics Chemistry, Am. Chem. Soc. meeting in Washington, 1962.

TABLE I

Copolymerization of Styrene and Fatty Esters at 70C
Experimental data of Harrison and Tolberg[c]

| Fatty ester or solvent | Styrene polymerized in 24 hr g[a] | Mol wt polymer | No. of Groups per Polymer Molecule | | | $r_s$[d] |
|---|---|---|---|---|---|---|
| | | | Styrene | Benzoate | Me Ester | |
| None | 20.0[b] | 49,000 | 470 | 2.6 | 0 | |
| Me stearate | 9.5 | 39,000 | 370 | 1.8 | 0.64 | 640 |
| Me oleate | 9.5 | 39,000 | 370 | 1.7 | 1.7 | 238 |
| Me *t,t*-10,12-octadecadienoate | 8.6 | 40,000 | 340 | 2.5 | 14.5 | 17 |
| Me alkali-conjugated linoleate | ...... | 33,000 | 280 | 1.0 | 12.1 | ...... |
| Me linoleate | 5.8 | 19,000 | 173 | 1.1 | 3.0 | 28 |
| Me linolenate | 4.0 | 13,400 | 125 | 0.9 | 1.1 | 61 |

[a] 10 g each of styrene and ester, 0.2 g benzoyl peroxide.
[b] 20 g styrene and 0.4 g benzoyl peroxide.
[c] From Fig. 1 in Reference (1).
[d] This calculation from equation (2).

show that stearate and oleate behave essentially as inert diluents, and that the unconjugated esters with more unsaturation are retarders. The molecular weights in Table I show that incorporation of all these esters in the polymer is largely or entirely due to chain transfer. However, the conjugated esters react with styrene mostly by copolymerization. Our calculations of $r_s$ values in Table I permit comparison of the relative reactivities of the various esters with styrene radicals (polymer radicals ending in $-CH_2-\overset{H}{\underset{Ph}{C}}\cdot$ units). $r_s$ is the ratio of the rate constants for the reaction of a styrene radical with styrene and with ester, respectively, and is determined (3) from the equation

$$\frac{-\Delta[S]}{-\Delta[E]} = r_s \frac{[S]}{[E]} + 1 \qquad 1.$$

The other quantities in the equation are defined in Table II.

In this paper, ester reactivities include reactions by both copolymerization and chain transfer. The reciprocals of the $r_s$ values are proportional to the relative reactivities of the esters with styrene radicals, with the relative reactivity of styrene monomer with styrene radical taken as unity. Thus, methyl 10,12-octadecadienoate is 14 times as reactive as oleate toward styrene radicals, etc. That methyl linoleate appears to be more reactive than the linolenate in Table I is probably due to experimental error.

The work of Harrison and Tolberg is the point of departure for our own. Our objectives were to obtain more accurate data near 70C, to determine whether higher temperatures would assist in incorporating more esters in polystyrene, and to investigate the copolymerization of methyl esters with acrylonitrile. Polar effects in copolymerization (3) suggest that the unsaturated fatty esters should be more reactive in copolymerizations with monomers containing conjugated nitrile, ester, or carbonyl groups.

## Experimental

*Methyl Esters.* Pure methyl oleate and methyl stearate were purchased from California Biochemicals Corp. Methyl linoleate, 96% pure, and methyl linolenate, 93% pure, were prepared by methanolysis of safflower seed oil and linseed oil, respectively, followed by urea-complex separation of the polyunsaturated esters. Conjugated methyl linoleate was prepared by alkali isomerization of the above methyl linoleate (4). Methyl eleostearate was prepared from tung oil, isomerized to the β-form, subjected to methanolysis, and purified by a combination of urea-complex formation and recrystallization at −42C. Due to isomerization during distillation, equilibrium mixtures of the α- and β-forms were used. Analyses for total eleostearate (5) varied from 90–98%.

*Polymerization Procedure.* Polymerizations were carried out at 60, 90, and 130C, in heavy 4-inch Pyrex tubes, using 1–3 ml aliquots of styrene or acrylonitrile and 1–10 fold volumes of esters, weighed as well as measured. Benzene was used in place of the esters for controls. The mixtures in the tubes were frozen and the tubes evacuated and flushed with nitrogen. Initiator was then added, and the tubes were reevacuated, sealed, and heated in an appropriate bath for 24 hr. At 60C the initiator was azobis-(2-methylpropionitrile), hereafter designated ABN; at 90C, *t*-butyl perbenzoate; at 130C, di-*t*-butyl peroxide.

TABLE II

Copolymerization of Styrene with Methyl Esters

| Methyl Ester | Styrene: Ester vol | $[S]_0$[a] | $[E]_0$[a] | Conversion wt % | Ester in polymer wt % | $-\Delta S$[b] | $-\Delta E$[b] | $r_s$[c] |
|---|---|---|---|---|---|---|---|---|
| 0.01M ABN; where marked* 0.1M ABN; 60C; 24 hr | | | | | | | | |
| Stearate | 1:1 | 26.13 | 7.98 | 23.5 | 0.7 | 11.41 | 0.024 | 190 |
| Oleate | 1:1 | 26.13 | 8.39 | 22.0 | 0.7 | 10.93 | 0.020 | 220 |
| Linoleate | 1:1 | 26.13 | 8.76 | 9.6 | 1.2 | 4.81 | 0.021 | 84 |
| | 1:1 | 8.71 | 2.97 | 27.9* | 1.1 | 4.72 | 0.017 | 140 |
| | 1:4 | 8.71 | 12.00 | 1.7 | 2.1 | 0.695 | 0.005 | 187 |
| | 1:4 | 8.71 | 12.13 | 6.5* | 2.4 | 2.74 | 0.024 | 113 |
| Linolenate | 1:1 | 8.69 | 3.05 | 6.3 | 2.2 | 1.06 | 0.0086 | 46 |
| | 1:1 | 8.69 | 2.89 | 21.3* | 1.4 | 3.04 | 0.0184 | 66 |
| | 1:4 | 8.69 | 12.33 | 2.9* | 2.2 | 1.24 | 0.0098 | 193 |
| Conjugated Linoleate | 1:4 | 8.69 | 11.77 | 5.0 | 21.7 | 1.67 | 0.164 | 13.7 |
| | 1:10 | 8.69 | 26.81 | 1.9 | 41.7 | 0.98 | 0.22 | 10.0 |
| | 1:4 | 8.69 | 12.16 | 11.8* | 26.0 | 3.76 | 0.47 | 12.4 |
| | 1:10 | 8.69 | 26.13 | 4.2 | 46.9 | 2.16 | 0.50 | 7.8 |
| | 1:1 | 26.07 | 8.89 | 17.6 | 8.7 | 8.23 | 0.28 | 11.5 |
| | 1:1 | 26.07 | 8.91 | 40.25* | 11.4 | 18.26 | 0.834 | 11.7 |
| | 1:1 | 26.07 | 8.90 | 35.3* | 8.2 | 16.55 | 0.527 | 16.0 |
| Mixture[d] | 1:1 | 16.90 | 5.93 | 11.5* | 12.1 | | | |
| 2.5 g/l *t*-Butyl Benzoate, 90C, 24 hr | | | | | | | | |
| Linoleate | 1:1 | 8.39 | 3.02 | 6.3 | 2.3 | 1.04 | 0.0088 | 45 |
| Conjugated Linoleate | 1:1 | 8.39 | 2.95 | 6.6 | 7.1 | 0.78 | 0.021 | 13.2 |
| | 1:4 | 8.39 | 12.24 | 1.0 | 17.5 | 0.363 | 0.027 | 18.3 |
| 2.5 g/l Di-*t*-butyl Peroxide, 130C, 5.75 hr | | | | | | | | |
| Linoleate | 1:1 | 16.79 | 5.91 | 36.6 | 3.9 | 11.79 | 0.168 | 42.0 |
| | 1:1 | 16.79 | 5.91 | 26.8 | 4.0 | 8.63 | 0.129 | 32.0 |
| Conjugated Linoleate | 1:1 | 16.79 | 5.91 | 48.1 | 12.6 | 14.06 | 0.723 | 12.1 |
| 2.5 g/l *t*-Butyl Peroxide, 130C, 24 hr | | | | | | | | |
| Linoleate | 1:4 | 16.79 | 23.63 | 7.9 | 11.8 | 5.72 | 0.263 | 35.1 |
| | 1:4 | 16.79 | 23.63 | 4.6 | 12.6 | 3.36 | 0.168 | 29.6 |
| Conjugated Linoleate | 1:4 | 16.79 | 23.64 | 19.3 | 30.8 | 11.15 | 1.76 | 12.0 |

[a] Mmol of initial styrene, [S], and ester, [E].
[b] Mmole of styrene and ester consumed in polymerization.
[c] Defined in equation 1.
[d] 75% by vol conjugated linoleate, 25% eleostearate.

TABLE III

Copolymerization of Acrylonitrile with Methyl Esters

| Methyl Ester | ACN:ESTER vol | $[A]_0$ [a] | $[E]_0$ [a] | Conversion wt % | Ester in polymer wt % | $-\Delta[A]$ [b] | $-\Delta[E]$ [b] | $r_a$ [c] |
|---|---|---|---|---|---|---|---|---|
| 0.01M ABN; except *, 0.1M ABN; 60C; 24 hr | | | | | | | | |
| Linoleate | 1:1 | 15.07 | 3.12 | 1.9 | 19.1 | 0.534 | 0.0227 | 4.66 |
| | 1:1 | 15.07 | 2.96 | 17.3* | 17.8 | 4.495 | 0.175 | 5.52 |
| | 1:4 | 15.07 | 11.93 | 4.4* | 22.7 | 2.77 | 0.146 | 6.85 |
| Linolenate | 1:1 | 15.07 | 2.78 | 17.7* | 18.9 | 4.37 | 0.183 | 4.78 |
| Conjugated Linoleate | 1:1 | 15.08 | 2.90 | 51.4* gel | 49.2 | 8.12 | 1.42 | 0.94 |
| | 1:1 | 15.08 | 3.00 | 76.6* | 48.5 | 12.51 | 2.12 | 1.08 |
| | 1:4 | 15.08 | 11.89 | 50.3* | 78.8 | 8.65 | 5.79 | 0.41 |
| | 1:10 | 15.08 | 29.67 | 29.2* | 82.9 | 9.67 | 8.50 | 0.34 |

[a,b,c] Have same significance as in Table II, except that A = acrylonitrile.

After reaction, the contents of the tubes were poured into methanol, and the residual polymer transferred quantitatively with the appropriate solvent. After thorough working with a spatula to extract monomer and ester, the precipitated polymer was separated by decantation, filtration, or centrifugation. The styrene polymers were dissolved in benzene; the acrylonitrile polymers, except those containing high proportion of ester, in dimethylformamide; the high-ester-content acrylonitrile polymers were benzene-soluble. The polymers were redissolved and reprecipitated four or more times. The benzene-soluble polymers were freeze-dried (6) at 0.5 mm pressure or less at 0C and finally at 60C. The dimethylformamide-soluble polymers were obtained in a flocculent form which was thoroughly washed with methanol and dried, first in a rotary evaporator, then at 0.1 mm or less at 100C. Infrared absorption showed that methyl stearate was completely separated from a mixture with polystyrene by the above procedure.

The filtrates from the workup of the polymers were concentrated and, after removal of the solvents, distilled quantitatively under vacuum to recover soluble polymers. The residues from the styrene reaction mixtures were very small (2–4% of the ester, including distillation hold-up), indicating little if any formation of low molecular weight polymers. Residues from acrylonitrile reaction mixtures were only slightly more.

The styrene-ester copolymers were analyzed by infrared spectroscopy, and the percent ester determined by comparison with standards consisting of polystyrene and pure methyl stearate. Both the standard mixtures and copolymers of unknown ester content were examined in $CCl_4$ solution, using 10% solutions and a 0.1 mm cell (except for high ester copolymer) and the carbonyl absorption band at 5.75 $\mu$. The procedure was reproducible within 0.3% ester.

The amount of acrylonitrile incorporated in the polymers was calculated from nitrogen analyses; nitrogen determinations on pure acrylonitrile agreed with the theoretical within 0.2%.

*Retardation by Methyl Eleostearate.* Three programs were undertaken in an effort to account for retardation of polymerization of styrene and acrylonitrile by methyl eleostearate.

1) A mixture of 0.879 g of ester and 0.905 g of styrene, 0.01 M in ABN, was heated for 24 hr in sealed, evacuated tubes at 60C. The mixture was distilled at reduced pressure and most of the ester was recovered. This recovered ester was retreated twice in the same manner with proportionate amounts of styrene and ABN. In each treatment, less than 5 mg of polymer was obtained. This experiment suggests that the retardation of polymerization is not due to a trace impurity in the ester.

2) On 72 hr heating with 1M ABN, methyl eleostearate alone yielded 32% of non-volatile residue having a molecular weight of 524, apparently a mixture of dimer with catalyst residues. Sixty-eight percent of methyl eleostearate of the original refractive index was recovered.

3) The last 60C experiment in Table II shows that replacement of 25% of conjugated methyl linoleate (in a mixture which would otherwise copolymerize readily) by methyl eleostearate results in retardation, but not cessation, of polymerization. The amount of ester found in the copolymer could be accounted for by the conjugated linoleate in the charge. Analysis of recovered ester indicated that, within experimental error, all of the eleostearate was recovered. Therefore the retarding properties of eleostearate are markedly reduced by dilution. However, in corresponding experiments with acrylonitrile instead of styrene as comonomer, no polymer at all was obtained in the presence of eleostearate.

## Results

Copolymerizations of methyl esters with styrene are summarized in Table II, with acrylonitrile, in Table III. In the copolymerizations with styrene, a different initiator, chosen for its appropriate half-life, was used at each temperature. The approximate half-lives are: 2,2′-azobis-(2-methylpropionitrile) (often designated as $\alpha,\alpha'$-azobisisobutyronitrile, here abbreviated to ABN), 17 hr at 60C (7); *t*-butyl perbenzoate, 50 hr at 90C (8); di-*t*-butyl peroxide, 3 hr at 130C (9).

Equation 1 is a modified form of the general copolymerization equation (3). It assumes that "ester radicals" react only with styrene monomer, never with ester monomer. This assumption is justified partly by the failure of esters to polymerize by themselves, partly by our efforts to determine the other monomer reactivity ratio, $r_e$, which was found to be zero within experimental error. Equation 1 applies strictly only at low conversions. Below 50% conversion, the equation applies satisfactorily if [S] and [E] are taken as the *average* concentrations of unreacted styrene and ester during the experiment. All of our results were calculated first on this basis. In some experiments at high conversions those results were compared with those calculated from the exact and integrated form of the equation:

$$\log\frac{[E]_0}{[E]} = \frac{1}{r_s-1}\log\frac{(r_s-1)\dfrac{[S]_0}{[E]_0}+1}{(r_s-1)\dfrac{[S]}{[E]}+1} \qquad 2.$$

Agreement was usually found to be satisfactory, but the $r_s$ values for experiments in Table II with conversions above 30% are from equation 2.

TABLE IV
Summary of Monomer Reactivity Ratios ($r_e = 0$)

| Methyl Ester | $r_s$ (Styrene) | | | $r_a$ (Acrylonitrile) 60C |
|---|---|---|---|---|
| | 60C | 90C | 130C | |
| Stearate | 190 | | | |
| Oleate | 220 | | | |
| Linoleate | 140 | 45 | 36 | 5 |
| Linolenate | 60 | | 30 | 5 |
| Conjugated Linoleate | 12 | 15 | 11 | 0.4 |

## Discussion

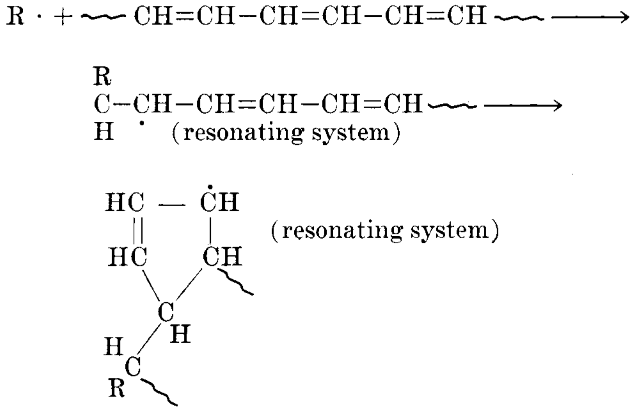
The results in Tables II and III are summarized in Table IV. The results with styrene at 60C are probably more reliable than those of Harrison and Tolberg (1), partly because the initiator contained no ester groups. The two sets of results are fairly consistent and the general conclusions drawn in the introduction are confirmed. From the $r_s$ values and equations 1 and 2, either $-\Delta[S]/-\Delta[E]$ or $[S]/[E]$ may be calculated when the other ratio is fixed or known. Considerable proportions of conjugated methyl linoleate can be incorporated in polystyrene.

The results with styrene at 90C and 130C indicate that incorporation of the least reactive esters is increased the most by the use of higher temperatures, but the unconjugated esters are still unreactive at 130C. $r_s$ for the conjugated linoleate is nearly independent of temperature. Thus, the low reactivity of conjugated linoleate compared with styrene (about 1/12) is not due to a difference in activation energy for addition of a radical, but to unfavorable steric factors. Internal double bonds are known to be much less reactive than terminal double bonds among unconjugated monomers for the same reason (3).

The $r_a$ values for acrylonitrile indicate that this monomer is much more suitable than styrene for copolymerization with unsaturated methyl esters. This result was expected because most unconjugated aliphatic monomers are also much more reactive with acrylonitrile than with styrene. However, Tables III and IV give numerical values for copolymerizations of acrylonitrile with methyl esters and permit calculations of copolymer compositions from feeds, and vice versa. An $r_a$ value of 5 means that an equimolecular mixture of acrylonitrile and methyl linoleate or linolenate would give a copolymer containing about 15 mole %, 48 wt %, of ester. A feed of 1 mole of nitrile and 2 of ester would give 22 mole %, 61 wt %, of ester in the copolymer, and so on, with 50 mole % of ester as the theoretical limit from very high ester feeds.

The conjugated linoleate is still more reactive; an acrylonitrile radical prefers conjugated linoleate over acrylonitrile by a factor of 2.5. Here an equimolecular mixture of the two monomers would give 42 mole %, 80 wt %, of ester in the copolymer, and so on.

Our experiments on the retarding properties of methyl eleostearate, described under Experimental, indicate that these properties are inherent in the ester at 60C, and that they become noticeably weaker with 12 vol % eleostearate in the feed than with 50% of this ester. The results in Table II indicate that this ester is reactive enough toward polymer radicals, but that the radical thus formed from eleostearate is too unreactive in chain propagation or too reactive in chain termination, or both. Addition of a polymer radical, R·, to the triply conjugated system might be expected to proceed as follows:



We suggest that the cyclic allyl radical just above has poor propagating or very good terminating properties. A similar radical should be formed by addition of a radical to cyclopentadiene. This hydrocarbon, or its derivaties, should also be a strong inhibitor of polymerization, but we know of no data on this point.

We now consider the implications of our results with methyl esters on the direct preparation of copolymers from linseed oil. The most studied monomer, styrene, is poor for the purpose. Isomerization of all the unconjugated double bonds to conjugated double bonds will make the former linoleate units moderately reactive in copolymerization with styrene, but will produce strongly retarding groups from the former linolenate units. Therefore, isomerization of linseed oil is unpromising unless formation of triply conjugated systems can be prevented or retarded, or unless they can be removed preferentially, as in a Diels-Alder reaction. Because styrene is so cheap and available, these requirements deserve at least some preliminary investigation.

Acrylonitrile is much more promising for copolymerizing with linseed oil. The linoleate and linolenate units are sufficiently reactive that conjugation (complicated by inhibition by triply conjugated systems) may not be necessary. The principal difficulty may arise from gelation due to copolymerization of two or more functional groups in the same oil molecule. However, variations among natural linseed oils, the use of chain transfer agents to retard gelation, or use of limited conversion may lead to a practical means of making a fairly high polymer, which is also a drying oil, containing at least 60–80 wt% of linseed oil. Whether such a polymer can ever be made by direct emulsion polymerization, or whether it can be emulsified after being made by oil-phase or bead polymerization, remains to be seen.

From copolymerization tables (3), we estimate that $r_a$ values for methyl acrylate will be about two-thirds as large as those reported here for acrylonitrile and thus somewhat more favorable for copolymerization. The ratios for methyl methacrylate will be about three times those for acrylate, and the ratios for methacrylonitrile will be about three times those for acrylonitrile. Thus the more substituted monomers are expected to copolymerize less easily with linseed oil acids.

In summary, our work with methyl esters of unsaturated $C_{18}$ fatty acids offers some leads for the utilization of linseed oil in copolymers and a new and improved basis for planning and understanding development work in this field.

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# Analog Computers and Kinetics of Hydrogenation[1]

**R. O. BUTTERFIELD, E. D. BITNER, C. R. SCHOLFIELD, and H. J. DUTTON,**
**Northern Regional Research Laboratory,[2] Peoria, Illinois**

## Abstract

Investigations of the kinetics of consecutive reactions frequently require complicated calculations to determine specific reaction rate constants from experimental data. Analog computers permit a convenient empirical adjustment of rate constants in kinetic equations to match experimental results. Once an electronic network analogous to the chemical reaction system is set up, specific reaction rates can be determined by adjusting potentiometers, which are the analogs of the rate constants, until an acceptable fit of calculated and experimental data is reached. Applicability of a small analog computer to the kinetics of hydrogenation is presented.

## Introduction

A SERIES OF calculations involving successive approximations is frequently required to arrive at an acceptable fit of experimental kinetic data and to determine the specific reaction rate constants (2). The application of digital computers to a study of the kinetics of hydrogenation has recently been described (4), but this procedure becomes awkward in experiments in which "isolinoleate" and the "oleate shunt" are considered and are studied with radioactively labeled intermediates (7).

Analog computers are ideally adapted for the solution of differential equations in chemical kinetics (6). Once an electronic network has been set up analogous to the kinetic equations, the problem of determining specific reaction rate constants consists merely in empirical adjustment of potentiometers, which are the analogs of the rate constants, until the desired fit of the experimental kinetic data is reached.

A small analog computer (9 amplifier, Heathkit *Educational Electronic* Analog Computer, Model EC-1) was applied to a variety of kinetic problems recently encountered in this laboratory in our research on kinetics of hydrogenation. Its successful use demonstrates that the gap between the fields of organic chemical research and electronic methods of computation can readily be bridged with a distinct advantage to research.

## Experimental Procedures

### Basic Computing Elements and Mathematical Operations

The following discussion is a simplification of analog computer operations based on Osburne's description (6). The fundamental component of an analog computer is its high-gain dc amplifier. The gain of this amplifier, which is represented by a triangular symbol (Fig. 1), ranges between ten thousand and several million, *depending upon* design and precision required; thus, an output of 100 v will frequently require an input of less than 10 mv. For mathematical purposes, this small input voltage may be considered as zero to simplify the algebraic equations.

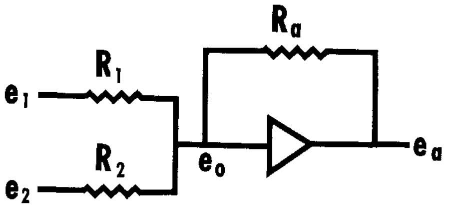

FIG. 1. Computer circuit for addition and multiplication.

Circuits for addition and multiplication, illustrated in Figure 1, operate as follows: The current through resistor $R_1$ is equal to the voltage drop divided by the resistance (Ohm's law); hence the current through $R_1$ is $\frac{e_1-e_o}{R_1}$, the current through $R_2$ is $\frac{e_2-e_o}{R_2}$, and the current through $R_a$ is $\frac{e_o-e_a}{R_a}$. The current through the feedback resistor, $R_a$, is equal to the sum of currents through $R_1$ and $R_2$ since no current passes through the amplifier or

$$\frac{e_o-e_a}{R_a} = \frac{e_1-e_o}{R_1} + \frac{e_2-e_o}{R_2}$$

Since $e_o$ as explained is essentially zero, then

$$-\frac{e_a}{R_a} = \frac{e_1}{R_1} + \frac{e_2}{R_2} \text{ or}$$

$$-e_a = \frac{R_a e_1}{R_1} + \frac{R_a e_2}{R_2}$$

If the ratios of resistors $R_a/R_1$ and $R_a/R_2$ are equal to 1, $e_1$ and $e_2$ have been added to give the voltage $e_a$ of negative sign. Also, if the ratios $R_a/R_1$ and $R_a/R_2$ are other than unity, the input voltages $e_1$ and $e_2$ have been multiplied by these ratios. Then $e_a$ becomes the sum of the product of $e_1$ multiplied by a constant and of $e_2$ multiplied by a constant; or, two incoming signals each multiplied by the ratio of the resistances have been algebraically added to give the negative output signal.

For multiplying by a positive constant less than 1 without an amplifier, a potentiometer is used as shown

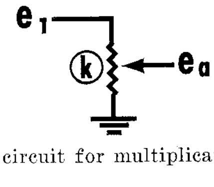

FIG. 2. Computer circuit for multiplication by less than 1.

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[1] Presented at the AOCS meeting in Toronto, Canada, 1962.
[2] A laboratory of the No. Utiliz. Res. & Dev. Div., ARS, U.S.D.A.