Typical calibration data are:

Actual He Flow (measured with) soap-film meter) cc/min	GM-LD Meter Deflection (divisions right)
8	12
16	19
24	24
31	28
38	32
46	35
53	38
59	42
66	44
72	47

This table or a plot from its data allows a quick and fairly accurate measurement of column flow without dismantling the FID assembly. The adjustable 50K resistance, when turned to its lowest value, restores the GM-LD to its former sensitivity.

Addition of this single potentiometer is a simple modification that has made the GM-LD in this laboratory a more useful instrument.

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Homogeneous Hydrogenation of Soybean Fatty Esters by the Ziegler Type of Catalyst Systems

It has already been shown that soybean oil esters are partially hydrogenated by such homogeneous catalysts as iron pentacarbonyl (1) and dicobalt octacarbonyl (2) or by such heterogeneous catalysts as palladium complexes (3), sodium borohydride-catalysts (4), and copper-chrome catalysts (5). Meanwhile hydrogenation of soybean methyl esters with metal acetylacetonate (abbreviated as $M[acac]_3$), such as $Ni(acac)_3$, $Co(acac)_3$, $Cu(acac)_2$, and $Fe(acac)_3$ activated by methanol, has been reported by Emken et al. (6).

Most of these catalysts promote the reduction of polyunsaturated fatty esters with positional and geometric isomerization of double bonds, and the degree of isomerization varies with the catalyst. But it has also been reported (7) that a number of transition metal compounds, for example, $Ti(O\ i\text{-}C_3H_7)_4$, $VO(O\ n\text{-}C_4H_9)_3$, $Cr(acac)_3$, etc., combined with organometallic derivatives are active catalysts for the hydrogenation of olefins (such as cyclohexene, 1-octene, etc.).

In this paper homogeneous hydrogenation of soybean fatty esters (methyl linoleate, methyl linolenate) by the binary catalyst systems of transition metal compounds and organo-aluminium compounds is reported. Transition metal compounds which were tried were $Ni(acac)_3$, $CoCl_2$, $Co(acac)_3$, and $FeCl_3$. Triethyl aluminum was used as an organo-aluminium compound.

A description of the hydrogenation reaction follows. In an autoclave (100 ml) were placed 1 mmol of transition metal compound, 5 mmol of $AlEt_3$, 50 ml of hexane (as a solvent), and 8.5 g of soybean oil methyl esters (methyl linoleate, methyl linolenate) under inert atmosphere. Then hydrogen was introduced up to 150 kg/cm^2. The hydrogenation reactions were carried out at 150C for 2 hr with vigorous agitation.

After the reaction the reduced products were analyzed directly after washing. Countercurrent distribution between *n*-hexane and acetonitrile was used to fractionate the reduced products. Individual fractions were monitored by GLC (2). For GLC a 200-ft column, coated with Apiezon L, was used with a Barber-Colman chromatograph equipped with a Radium D ionization detector. The operation was carried out at 175 C with a nitrogen flow of 35 ml/min. The percentage of isolated *trans* double bonds in the hydrogenated products was determined by comparing the IR absorption of the methyl esters in a carbon disulfide solution with the 10.36 mμ region with that of methyl elaidate. The diene conjugation was measured by UV absorption in the 231–234 mμ region.

Table I shows the results of the hydrogenation reaction of soybean methyl esters. With each catalyst system (1–4) the contents of triene and diene in the reaction products were decreased and the content of monoene was increased with the reaction time. The content of saturated esters (stearate, palmitate) remained constant. Table II shows the results of the hydrogenation of methyl linoleate and methyl linolenate. The same tendency is observed in Table II as in Table I. The decrease in diene and triene and the increase in *trans* unsaturation are related to the degree of hydrogenation. There was essentially no monoene hydrogenation to saturated; only a trace of stearate was formed. During each hydrogenation reaction only a small accumulation of conjugated dienes was observed.

From these results the conjugated dienes which were formed during the reaction may be considered intermediates. The scheme via conjugated dienes is presumed to be like that of Frankel (2):

trienes → dienes → conjugated dienes → monoenes

As for the reduction mechanism, the following

TABLE I

Hydrogenation of Soybean Fatty Esters[a]

Catalyst systems[b]	Palmitate (%)	Stearate (%)	Monoene (%)	Diene (%)	Triene (%)	IV (calculated	Conj. diene (232 mμ)	*trans* (%)
S	10.9	4.1	25.4	52.1	7.5	132.0	0	0
1	10.5	4.0	48.2	34.5	2.8	108.0	1.15	19.4
2	10.5	4.2	62.6	21.5	1.2	92.5	1.28	30.3
3	10.7	3.8	64.6	20.1	0.8	90.1	1.01	48.5
4	11.0	3.9	71.3	13.8	trace	82.5	0.50	49.2

[a] The reactions were carried out at 150C for 2 hr (hydrogen pressure of 150 kg/cm^2); 1 mmol of transition metal compound, 5 mmol of $AlEt_3$, 50 ml of hexane as solvent, and 8.5 g of soybean methyl esters were used in each experiment.

[b] Catalyst systems: 1. $FeCl_3 \sim AlEt_3$; 2. $CoCl_2 \smile AlEt_3$; 3. $Co(acac)_3 \smile AlEt_3$; 4. $Ni(acac)_3 \sim AlEt_3$.

TABLE II

Hydrogenation of Methyl Linoleate[a]

Catalyst systems	Stearate (%)	Monoene (%)	Diene (%)	Conj. diene (%) 232 mμ	*trans* % as Elad- iate
1	0.1	69.5	30.4	3.85	21.5
2	0.2	75.5	24.3	1.03	34.4
3	0.0	80.3	19.7	2.05	38.8
4	0.4	89.0	10.6	2.10	51.7

Hydrogenation of Methyl Linolenate[a]

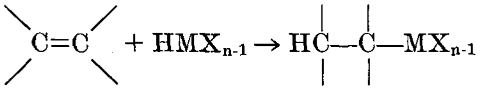
Catalyst systems	Stearate (%)	Monoene (%)	Diene (%)	Triene (%)	Conj. diene (%) 232 mμ	*trans* % as Elad- iate
1	0.0	53.1	29.1	17.8	3.82	30.3
2	0.0	64.8	22.7	12.5	4.01	35.7
3	0.0	68.2	21.2	10.0	2.04	38.9
4	0.0	74.9	17.5	8.5	1.85	43.2

[a] Reactions were carried out at 150 C for 2 hr under a hydrogen pressure of 150 kg/cm². Catalyst systems (1–4) and solvent were the same as in Table I; 8.5 g of methyl linoleate (or methyl linolenate) were used in each experiment.

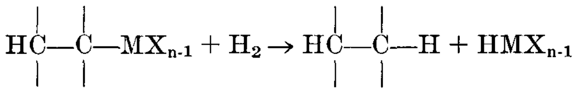
steps are postulated, as suggested by Sloan et al. (7). The reaction of transition metal derivatives with aluminum alkyls has, as its first step, alkylation of the transition metal derivative [1]. This is followed by hydrogenolysis of the metal-alkyl bond to yield a metal hydride [2], which then, added to an olefin, forms a new metal alkyl [3]. Hydrogenolysis of the latter yields saturated hydrocarbon with regeneration of the metal hydride [4].

$$R_3AlX + MX_n \rightarrow R_2AlX + RMX_{n-1} \quad [1]$$

$$RMX_{n-1} + H_2 \rightarrow RH + HMX_{n-1} \quad [2]$$



[3]



$$HC{-}C{-}MX_{n-1} + H_2 \rightarrow HC{-}C{-}H + HMX_{n-1}$$

[4]

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Paint Driers-Effect of Organic Acid Carrier

The effect, mechanism, and faster drying rates imparted to surface coatings by the metal portion of paint driers have been covered extensively in textbooks (1–3) and other publications. The organic acid carrier for the metal has also been described; however, little information has been published on the direct effect that this portion of the drier system exerts on the drying rate. Under carefully controlled conditions, studies have been conducted to determine what effect, if any, the acid carrier plays in the drying process. In this evaluation, naphthenic acid (4) and neo-decanoic acid (5) (a synthetic *α,α*-disubstituted monobasic acid containing 10 carbon atoms) were used as the organic acid carriers.

In all tests, the three enamel formulations which contained the neo-acid driers dried faster than similar paints which contained corresponding amounts of naphthenate driers. The differences in drying rates effected by the neo-acid and naphthenic acid driers were quite significant in some tests and marginal in others, depending on the particular paint formulation.

Two drier systems were evaluated with the cobalt soap as the sole drier in one test and a combination of cobalt and lead soaps in the second. The cobalt and lead naphthenates were obtained commercially; the corresponding neo-acid driers were prepared by a laboratory procedure similar to that used in the commercial production of naphthenate driers (6).

The drier systems were evaluated in the long- and medium-oil alkyd test enamel formulations shown in Table I. The results of this study are summarized in Table II and show that the type of organic acid carrier does affect drying time. Paint driers prepared with the synthetic neo-acid offer faster drying

TABLE I

Test Enamel Formulations

(Modified formulations based on "starting-point" formulae recommended by Reichhold Chemicals Inc.)

	I		II		III	
	Weight	Volume	Weight	Volume	Weight	Volume
TiO_2 R-900[a]	309.5	8.8	301.2	8.6	301.5	8.6
Kadox 515[b]	....	......	25.7	0.6	15.1	0.3
Syntex 40[c]	....	......	....	......	548.8	62.6
Beckosol P-296-70[d]	....	......	489.9	61.2	....	......
Beckosol P-670-55[e]	522.2	69.2	....	......	....	......
Nuosperse 657[f]	....	......	3.5	0.5	....	......
Varsol 1[g]	....	......	179.7	26.7	134.6	20.0
VM&P naphtha[g]	168.3	26.4	....	......	....	......
	1000.0 lb	104.4 gal	1000.0 lb	97.6 gal	1000.0 lb	91.5 gal
Weight/Gallon	9.58 lb		10.24 lb		10.93 lb	
PVC	22.3%		19.2%		15.6%	
NVM	59.7%		67.3%		73.9%	
Pigment/Resin solids ratio	1.078/1.000		0.953/1.000		0.740/1.000	

[a] E. I. duPont de Nemours and Company.
[b] Zinc oxide (N. J. Zinc Company).
[c] Long-oil soya alkyd (Jones-Dabney Company).
[d] Long-oil soya alkyd (Reichhold Chemical Company).
[e] Medium-oil linseed alkyd (Reichhold Chemical Company).
[f] Wetting agent (Nuodex Division of Tenneco Chemicals Inc.).
[g] Humble Oil and Refining Company.