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## Aldehydic Materials by the Ozonization of Vegetable Oils<sup>1</sup>

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OZONIZATION of oleic acid to produce azelaic and pelargonic acids is a well-known commercial process (3). These acids, which are used for preparing various synthetic lubricants and plasticizers, result from oxidative decomposition of the ozonolysis products. Alternatively, reductive decomposition either with zinc and acetic acid or with hydrogen over a palladium-charcoal catalyst produces aldehydic materials. This paper discusses the preparation of various aldehydic compounds by the ozonization of unsaturated vegetable oil products followed by reductive decomposition of the ozonolysis products and summarizes the research carried out for the past several years at the Northern Laboratory.

The ozonization of monounsaturated compounds will be described first, followed by a discussion of polyunsaturated compounds and the more complex unsaturated vegetable oil systems. Reactions and potential uses for these aldehydic compounds will then be considered.

### Ozonization of Methyl Oleate

*Effect of Solvent.* Reductive decomposition of the ozonolysis products obtained from methyl oleate gives the products pelargonaldehyde and methyl azelaaldehyde. This reaction has been known and used for many years, but results were complicated by the presence of side reaction products and yields have been generally low (41). The best preparative method gave 60-70% yields, and consisted of ozonization in

acetic acid followed by reaction with zinc (25). Distillation of either freshly prepared or stored reaction product gave residues which were apparently the aldehyde trimers.

Recently, Criegee and coworkers elucidated the mechanism of the ozonization reaction and the types of products obtained in different solvents (16). This work has been reviewed in a general review of the ozonization of organic compounds (5). Alcohols, particularly methyl and ethyl alcohols, as participating or reactive solvents are apparently to be preferred.

In our investigations with methyl oleate, methanol proved to be the best solvent (Table I) (31). Methanol reacts somewhat with ozone, and this secondary reaction accounts for the 21% in excess of theory ozone consumed. The products of this secondary reaction do not interfere in the oximation analyses for carbonyl or isolation of carbonyl compounds (24); however, they apparently do interfere in chromatographic analyses (9). The ozone uptake is essentially quantitative, only 1-2% escaping near the end of the reaction. As measured before isolation of products, the conversion of unsaturation to carbonyl compounds was 92-93% of theory. Temp of the ozonization within the range of -20 to +25C had little effect. The yield of crude product after isolation by distillation was 94%, and its purity was in excess of 90%. The principal impurity was dimethyl acetal of methyl azelaaldehyde. In other runs where care was taken to minimize acetal formation, purities were even higher.

With acetic acid a product of high purity was obtained but in low yields. The low yield may have resulted from the presence of acidic compounds during isolation of the products by distillation. We found in several preparations that all traces of acidity must be removed to prevent high residues resulting from distillation.

The superiority of methanol as a medium for ozonization has also been demonstrated when oxidative cleavage is used for analytical purposes (1). Not more than 3-5% chain degradation occurred, in contrast to the large amount of degradation that occurred with other solvents.

The explanation for the superior results obtained in methanol depends on the Criegee mechanism for ozonization (Fig. 1). The primary ozonide, evidence for which exists only for *trans* di(*tert*-butyl)-ethylene (18), immediately forms a transient intermediate called a zwitterion (I) and a carbonyl compound. The zwitterion may then react in any one of several dif-

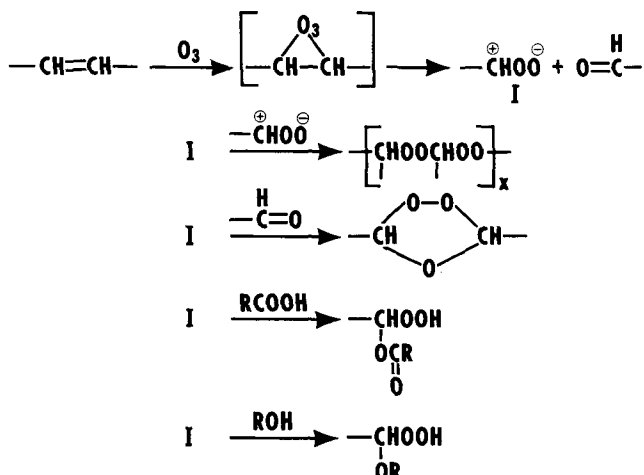


Fig. 1. Criegee mechanism for ozonization.

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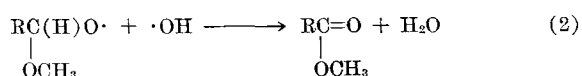
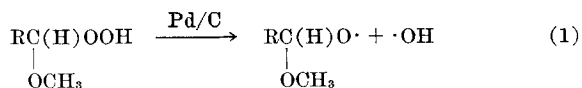
TABLE I  
 Ozonization of Methyl Oleate and Reductive Decomposition of Its Ozonolysis Products

Solution	Ozone consumed percent of theory	Temp of ozonization C	Temp of reduction C	Carbonyl conversion %	Methyl azelaaldehyde product	
					Yield, %	Purity, %
By Zinc and Acetic Acid						
Methanol.....	.....	-20	30-35	92	94	90
Methanol.....	121	+25	30-35	93	.....	.....
Methylene chloride.....	105	-22	30-35	72	76	87
Methylene chloride.....	132	-25	30-35	72	66	.....
Acetic acid.....	110	+34	30-35	.....	64	93
By Hydrogen Over Palladium on Charcoal						
Methanol.....	115	-20	0	78	85	84
n-Butanol.....	98	-20	0	63	.....	.....
Propionic acid.....	113	-27	8	81	44	71
Ethyl acetate.....	107	-23	26	.....	87	75
Ethyl acetate + 20% methanol.....	110	-23	8	.....	76	.....
Ethyl acetate + 20% acetic acid.....	114	-15	35	.....	93	87
n-Heptane + 50% ethanol.....	120	-27	23	68	60	.....
n-Heptane + 20% t-butanol.....	141	-14	50	.....	67	.....

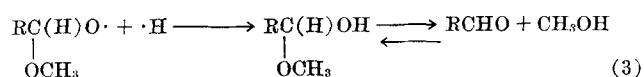
ferent ways, depending upon the solvent present. In methanol, a methoxy hydroperoxide is formed. In acetic acid, a mixture of acetoxy hydroperoxides and polymeric peroxides is formed (6). In inert solvents, the zwitterion may react with the carbonyl compound formed during the cleavage reaction to produce an ozonide. Alternatively, it may react with itself to form dimeric, trimeric, or higher polymeric peroxides. These polymeric peroxides react with difficulty (9,17). Rigorous conditions are necessary and various side reactions, including chain degradations, are apt to occur.

**Effect of Reduction Method.** Methanol gave superior results when the ozonolysis products were reduced with zinc and acetic acid. When hydrogenation over palladium on charcoal was used, yields were considerably lower; furthermore, it was impossible to purify the methyl azelaaldehyde easily by distillation as it was with the zinc-reduced product. Apparently the impurities had boiling points too near that of methyl azelaaldehyde for effective separation, or perhaps an azeotrope was formed.

Examination of the methyl azelaaldehyde product showed the major impurity to be dimethyl azelate. Its presence in 15-23% concentration indicated 30-46% decomposition of the methoxy hydroperoxide to the methyl ester. (Presumably one-half of the bifunctional portions of the ozonolysis products are already present as the aldehyde ester, and one-half as the methoxy hydroperoxide, in accordance with the Criegee mechanism.) Such a decomposition on the catalyst surface may have occurred as a result of homolytic cleavage involving dehydration in the following way (39):

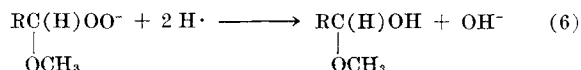
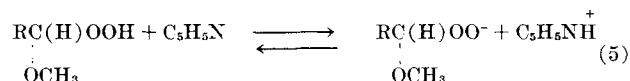


The desired reduction with an activated form of hydrogen is indicated in the following equations:



It was possible to reduce the undesired by-product reaction considerably by the use of pyridine (Table

II) (33). When pyridine amounted to 10% by wt of the solvent, it also prevented hydrogenation of residual olefinic unsaturation in partial ozonization. Furthermore, if pyridine was present during the ozonization as well as the hydrogenation step, it eliminated the small amount of acetal formation that usually occurred. Pyridine may minimize homolytic cleavage of the methoxy hydroperoxide. The hydroperoxide anion is then not subject to homolytic cleavage but is really reduced by hydrogen:



### Homologous Aldehyde Esters

The monounsaturated starting material used for the ozonization reaction may be varied depending upon the particular aldehyde ester desired. Thus, methyl oleate gives the C-9 aldehyde ester; methyl eicosenoate, the C-11; and methyl erucate, the C-13. The C-20 and C-22 monounsaturated acids are present in relatively high concentration in mustard and *Crambe abyssinica* seed oils. The yields of carbonyl compounds before isolation of the products are as good as those for methyl oleate (Table III) (30). However, the small-scale operation and the high temp required for distillation (which resulted in polymer formation) gave lower isolation yields. For many purposes, distillation may not be required, so that full advantage of the high yields might be realized.

Another potential route to homologous aldehyde esters lies in the partial ozonization of polyunsaturated esters. Thus, the bifunctional fragments to be expected from methyl linoleate would include the C-12 aldehyde ester as well as methyl azelaaldehyde. Similarly, the fragments from methyl linolenate

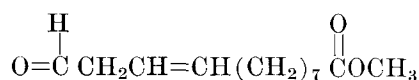
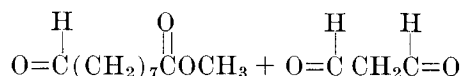
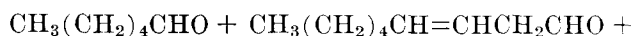
 TABLE II  
 Catalytic Hydrogenation Over Palladium on Charcoal  
 Effect of Pyridine on Product Purity  
 (GLC Analyses)

Component	Product composition, wt % resulting from ozonization in		
	Methanol	Methanol-pyridine	Methylene chloride-pyridine
Methyl azelaaldehyde.....	68.4	88.7	56.6
Methyl azelaaldehyde dimethyl acetal.....	1.9	0	.....
Dimethyl azelate.....	23.6	7.1	.....
Pelargonaldehyde.....	1.3	1.1	1.8
Unidentified.....	4.8	3.1	41.6

TABLE III  
Preparation of Homologous Aldehyde Esters

Material ozonized		Ozone consumed, % of theory	Isolated yield, %	Product		
Methyl ester	Amount (g)			Composition, %		
				C-9	C-11	C-13
Oleate.....	120	120	94	90.5	....	....
Eicosenoate.....	10	117	58	0.8	90.4	5.6
Erucate.....	17.6	122	75	....	5.6	94.4

should include the C-15 and C-12 aldehyde esters. These polyunsaturated C-18 acids or esters are readily available by liquid-liquid centrifugal extractions (7,8). The products to be expected from the partial ozonization of methyl linoleate are:



The course of the ozonization reaction was followed at periodic intervals by withdrawing samples, reducing them, and running GLC analyses (30). In the ozonization of methyl linoleate after about 60% of theory ozone consumption (50% of double bonds attacked), the product contained about 54% of methyl azelaaldehyde, 18% of methyl 11-formyl-9-undecenoate, and 28% of unreacted starting material. With recycling of methyl linoleate, yields at 60% ozone consumption would approach 75% of methyl azelaaldehyde and 25% of methyl 11-formyl-9-undecenoate. At 30% ozone consumption, yields would approach 68% and 32%, respectively.

Similar results are obtained with methyl linolenate. At about 30% ozone consumption, the following conversions (potential yield figures in parentheses) were obtained: methyl azelaaldehyde, 24% (50%); methyl 11-formyl-9-undecenoate, 12% (25%); and methyl 14-formyl-9,12-undecadienoate, 12% (25%).

The higher aldehyde esters cannot be separated readily from unreacted starting material by fractional distillation, but can be separated easily through the sodium bisulfite adduct. The unsaturated aldehyde esters can be hydrogenated to the more stable saturated compounds over palladium on charcoal catalyst. Conversion of the aldehyde group to an acetal also increases the stability of the mol without decreasing its effectiveness in many reactions.

### Ozonization of Unsaturated Vegetable Oils

The ozonization of an unsaturated vegetable oil results in the formation of a number of products

TABLE IV  
Ozonization of Soybean Oil, Margarine, and Triolein Reductive Decomposition with Zinc and Acetic Acid

Material ozonized/solvent	Ozone consumed, Percent of theory	Total carbonyl conversion (%)	Carbonyl yield of aldehyde oil (%)
Soybean oil			
Methanol.....	135	48	77
Methylene chloride.....	125	45	78
Ethanol.....	124	59	86
Ethyl acetate-methanol (80:20).....	127	56	92
Methylene chloride-methanol (55:45).....	130	60	91
Margarine			
Methylene chloride-methanol (55:45).....	129	75	91
Triolein			
Methylene chloride-methanol (55:45).....	129	84	85

including propionaldehyde, caproaldehyde, pelargonaldehyde, malonaldehyde, and azelaaldehydic acid, which is retained as the glyceride ester. This product we call an "aldehyde oil." Ideally, the structure of an aldehyde oil would be the triglyceride of azelaaldehydic acid. In reality, this structure can never be realized directly from natural oils because of the saturated fatty acids present in varying degrees.

Unfortunately, methanol is not a good solvent for vegetable oils, and ozonization of soybean oil in methanol did not give the hoped-for results (Table IV) (32). However, the use of methanol in combination with another good solvent, such as ethyl acetate and methylene chloride, gave excellent results. The total conversion of unsaturation to carbonyl compounds was low because of the formation and destruction of malonaldehyde by ozone. Thus, the actual yield of useful aldehyde products should be about 57 mole % or about 99 wt % of the original soybean oil. With use of the solvent combinations described, carbonyl yields of 56-60% and wt recovery averages of over 90% were actually obtained. The carbonyl conversion can actually be improved by the use of partially hydrogenated oils, such as margarine, which gave 75% carbonyl conversion, or by the use of triolein, which gave 84% conversion. The improved conversions are the result of a lower degree of polyunsaturation and less formation of malonaldehyde. The decomposition of malonaldehyde could be followed by the formation of acidic compounds:

Ozone consumed, % of theory	Yield of acidic compounds, %
94	12.9
98	16.5
127	22.2
151	31.1

Under similar conditions, the maximum acidity developed by methyl oleate was 2-3%.

### Partial Ozonization of Unsaturated Vegetable Oils

Monoaldehyde and dialdehyde oils can be prepared by the partial ozonization of unsaturated vegetable oils (34). Reduction of the ozonolysis products by zinc gives aldehyde oils with residual unsaturation. Reduction by catalytic hydrogenation gives poor yield of aldehyde oil as well as saturating the oil to a large extent. However, hydrogenation in the presence of pyridine gave good carbonyl yields without attendant hydrogenation of the double bonds. By this means, oils approximating mono- and dialdehyde oils have been prepared.

### Reactions of and Uses for Azelaaldehydic Acid Derivatives

*Previous Work.* Azelaaldehydic acid and its derivatives have been used to prepare omega-amino compounds as intermediates for nylon-9 by several investigators (13,26,27,28,29). Other routes to the omega-amino compounds that involve ozonization are also available (12). Although the polyamides from dibasic acids and diamines having an even number of carbon atoms give higher melting points than those having an odd number of carbon atoms, the reverse is true for the polyamides from amino acids (22). Thus, the polyamide from 9-aminononanoic acid has a higher melting point than either the polyamide from the 8- or 10-carbon amino acid (14). Nylon-11 is produced commercially in France from castor oil and has met with considerable success apparently because of its low moisture absorption (4). Nylon-9

has a higher melting point than nylon-11, has comparable moisture absorption (2), and would appear to be a promising outlet for azelaaldehydic acid compounds.

A polyester having a low melting point (64–66°C) has been prepared from 9-hydroxynonanoic acid that was made by reducing methyl azelaaldehyde (23).

Omega-cyclohexyl fatty acids prepared *via* the condensation of cyclohexyl magnesium bromide with methyl azelaaldehyde and other aldehyde esters showed bactericidal activity (21). The homolog of acitiazic acid prepared from ethyl azelaaldehyde apparently showed no biological activity (15). The unsaturated dibasic acid prepared by the condensation of malonic acid with azelaaldehydic acid is a homolog of traumatic acid, which incites tumors in the tomato plant (10). The homolog does not inhibit germination of wheat germ, as does traumatic acid, but is an active plant wound hormone (19).

Various aldehydic acids including azelaaldehydic acid have been used to prepare resins claimed to be useful in coating compositions for laminating paper, cloth, wood and glass, and as plasticizers for other resins by condensation with diamines (11).

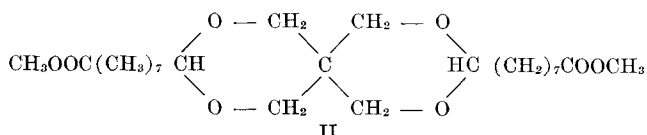
Acetal esters of the 3-, 4-, and 5-carbon aldehydic acids reduce the amount of frothing agent required to obtain good froths with mineral pulps (20).

*Northern Laboratory Work.* Methyl azelaaldehyde is stable indefinitely when stored under nitrogen and refrigerated. Conversion of the air-sensitive aldehyde group to an acetal increases stability in air. The dimethyl acetal of methyl azelaaldehyde can be prepared readily in good yield from methanol in the presence of an acidic catalyst (33). The acetal ester undergoes alcoholysis reactions at either functional group depending upon the catalyst used (38). The use of potassium acid sulfate results in alcoholysis at the acetal group, whereas the use of sodium methoxide results in alcoholysis of the ester group (Fig. 2). One exception to the selectivity is the reaction with allyl alcohol, which reacts with both acetal and ester functions in the presence of potassium acid sulfate.

Acetals react at elevated temp over an acid catalyst to form alkenyl ethers by splitting out alcohol.

Various acetal-esters of azelaaldehydic acid prepared as described above are being evaluated as plasticizers.

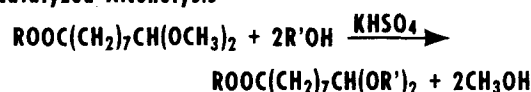
One of the most interesting acetals of methyl azelaaldehyde is the pentaerythritol acetal:



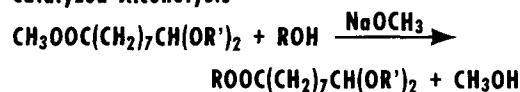
This diester can be hydrolyzed quantitatively to the dibasic acid with no effect on the acetal linkage. Such bifunctional compounds react with glycols and diamines to form poly(ester-acetals) and poly (amide-acetals), which constitute a new class of polymers. In these polymers, there are two different functional groups present in the polymer backbone (35–37).

The poly(ester-acetals) are formed under the usual conditions for polyesterification. The diester II, either alone or with another diester, is heated with the diol to effect glycolysis with distillation of methanol in a nitrogen atmosphere and in the presence of

### A. Acid Catalyzed Alcoholysis



### B. Alkali Catalyzed Alcoholysis



R = methyl, n-butyl, 2-ethylhexyl, ethylene

R' = methyl, n-butyl, ethylene, glyceryl, pentaerythritol

### C. Cracking

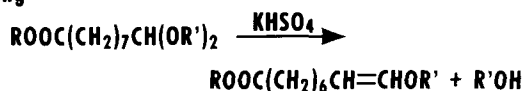


FIG. 2. Reactions of Methyl 9,9-Dimethoxynonanoate.

an alkaline catalyst. Heating is continued at elevated temp under a vacuum and with agitation supplied by nitrogen introduced through a capillary until the desired melt viscosity is attained. The poly(ester-acetals) and interpoly(ester-acetals) prepared in this manner are opaque, white solids that vary in degree of hardness according to the ratio of diesters used (Table V).

These poly(ester-acetals) have the unique property of undergoing crosslinking in the presence of certain catalysts including litharge, antimony oxide, zinc oxide, and zinc acetate. The crosslinked products are transparent, swell but do not dissolve in organic solvents, melt only at ignition temp, and are strongly adherent to glass. The time required for the crosslinking reaction depends upon mol wt and temp. In one example with litharge, crosslinking was complete within 23 min at 270°C. Adhesion to glass was incomplete in interpoly(ester-acetals) containing a ratio of II to dimethyl terephthalate (III) of 10:90, but was complete at ratios of 20:80 and higher.

The poly(amide-acetals) can be prepared from either the diester I or the dibasic acid. The polymers obtained from condensation with hexamethylene diamine have a melting range of 160–163°C. Interpolymers with dimethyl azelate had melting ranges up to 100°C, depending upon the concentration of dimethyl azelate and upon the ratio of amine end groups to carbomethoxy end groups (Tables VI, VII). The use of ethylene diamine in place of hexamethylene diamine gave products having higher melting points. With no dibasic acid other than II present, the resulting homopolymer and melting ranges of 175–180°C. For an interpolymer containing 9.3% of II with dimethyl azelate (IV), a melting range of 232–235°C was obtained.

The homopoly(amide-acetals) and interpoly(amide-acetals) also crosslinked when heated with catalysts to give transparent, insoluble, and infusible solids

TABLE V

Interpoly(ester-acetals) from II, Dimethyl Terephthalate (III), and Ethylene Glycol

Ester ratio II/III	Catalyst	Product characteristics			
		Melting range (°C)	MW/n	Limiting viscosity number	Description
0/100	CaO	242–246	.....	.....	Hard, brittle
10/90	CaO	215–219	10860/49	16.5	Hard, brittle
20/80	Na <sub>2</sub> CO <sub>3</sub>	188–194	4940/16	6.7	Hard, tough
30/70	CaO	141–155	1645/6	.....	Flexible, tough
100/0	CaO	87–88	16100/35	.....	Hard, brittle

TABLE VI  
Interpoly (amide-acetals) from II,  
Dimethyl Azelate (IV), and Hexamethylene Diamine

Ester ratio II/IV	Product characteristics			
	Melting range (C)	MW/n	Limiting viscosity number	Description
0/100	215-217	5195/19	43.0	Hard, brittle, opaque
5/95	200-202	4940/17	21.2	Hard, brittle, opaque
10/90	193-196	6300/21	15.4	Hard, brittle, opaque
20/80	185-187	5260/17	11.3	Hard, brittle, opaque
35/65	173-177	2000/6	.....	Hard, brittle, opaque
50/50	161-163	5525/14	.....	Hard, brittle, opaque
75/25	162-165	7890/17	.....	Hard, brittle, translucent
100/0	160-163	3030/6	.....	Hard, brittle, opaque

that adhered strongly to glass. Thus, the homopoly (amide-acetal) crosslinked in 20 min at 260C by using excess p-toluene sulfonic acid.

A number of exploratory tests have been made on aldehyde oils to determine their reactivities in typical condensation reactions (32,40). Generally, soft, flexible, insoluble, and infusible solids were obtained.

"Tri" aldehyde oils reacted fairly readily with phenol under alkaline conditions. Under acidic conditions, they reacted only with prolonged heating. However, they reacted readily with resorcinol under acidic conditions. If excess resorcinol was present, a hard, brittle, solid resin was obtained in contrast to the usual rubbery gel. When a hard, fusible resin from pelargonaldehyde and resorcinol was further heated with aldehyde oil, a flexible insoluble, and infusible resin was obtained. Although pelargonaldehyde gave no apparent reaction with urea, aldehyde oil gave a reaction almost immediately. An orange, rubbery gel was obtained with various reactant ratios.

A dialdehyde oil reacted with anhydrous hydrazine in ethanol solution formed an amber rubbery fracticelike material in 10-15 min (40). The product was insoluble in most organic solvents, but showed slight solubility in chloroform, xylene, and benzene. Reactions with other diamines, including p-phenylene and m-phenylene, and ethylene diamine, gave resilient products with poor tensile strength. Ortho-phenylene diamine gave a dark, sticky mass. These products were typically insoluble in most organic solvents and, except for the product from o-phenylene diamine, infusible.

Work is in progress to obtain linear, soluble, polymeric products having higher mol wt.

### Summary

Aldehyde esters of different chain lengths and aldehyde oils of various aldehyde contents were prepared from unsaturated vegetable oil products by complete or partial ozonolysis followed by reductive decomposition. Best yields (90% and better) were obtained when methanol was used as a participating solvent. Reductive decomposition with zinc and acetic acid gave a minimum of side reactions compared to catalytic hydrogenation over palladium on charcoal.

TABLE VII  
Effect of Amine-Carbomethoxy End-Group  
Ratio on Melting Points of Interpoly (amide-acetals)

Ester ratio II/IV	Mol wt	Amine/carbo-methoxy ratio	Melting range (C)
5/95	4900	2	200-202
	5400	0.03	189-191
	6000	36	193-195
	6200	0.0125	180-182

Proper modification of the catalyst resulted in nearly equivalent results.

Simple, bifunctional aldehyde esters may serve as intermediates in various nylon-type products. A new class of polymers prepared from the pentaerythritol acetal of methyl azelaaldehyde can be crosslinked rapidly in the presence of certain metal oxides or salts.

Polyfunctional aldehyde oils are extremely reactive and undergo a number of condensation reactions with diols and polyols, phenols, urea, and diamines. The products obtained are typically insoluble and infusible but are resilient solids.

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