Silicones with an ethoxy content of from 15 to 25% formed optimum copolymers with the alkyd resins—i.e., no processing difficulties, good compatibility, and superior thermal stabilities. Evidently there is an optimum range of silicone chain length and functionality which permits a more uniform distribution of the alkyd and silicone chains in the coploymer and results in a resin which best combines the properties of the two components.

Aryl silicones produce silicone-alkyd resins of superior thermal stability but of limited flexibility and adhesion. On the other hand, alkyl aryl silicones produce silicone-alkyd resins of superior flexibility, adhesion, and impact resistance. However, these properties were improved at a considerable sacrifice in thermal stability, gloss, and gloss retention, which are important properties in high-temperature surface coatings.

Some copolymers made during this investigation were superior with respect to maximum service temperature and at least equal in other properties to any known commercial product.

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Air Oxidation of 12-Tricosanone

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THE OXIDATION of long-chain paraffins with gaseous mixtures containing molecular oxygen has been the subject of many articles and patents (*13-16*). Less is known about the course of oxidation of long aliphatic chains containing functional groups although such molecules, and ketones in particular, are important because they are the primary or secondary derivatives in paraffin oxidation (*4*) and give rise to the complex products found in industrial wax oxidation.

Ketone oxidations have been carried out on molecules containing relatively short alkyl chains at conditions usually much less severe than those used for wax oxidation (*2, 3, 8, 10*). To study the effect of oxygen on a long paraffin chain containing an isolated carbonyl group, 12-tricosanone was oxidized with air in the presence of manganese napthenate catalyst at 160° C. Various fractions of the product, obtained by chromatographic separation over silica gel, were examined for the presence of free and esterified mono- and dibasic acids. The product was also reduced with lithium aluminum hydride and analyzed for alcohols and glycols. The material blown overhead during the oxidation was distilled and found to contain acids, paraffins, and *n*-octanal.

EXPERIMENTAL

Oxidation of 12-Tricosanone. One hundred grams of the ketone (Armour & Co., recrystallized from methanol, melting point, 67-8° C.) and 2 ml. of 6% manganese napthenate in naptha were heated to 150° C. in a 250-ml. flask which was 2 inches in diameter and had a 1.5-inch dispersion disk at the bottom. Dry air was passed through the vigorously stirred melt at 2 cubic feet per hour and the temperature climbed to 160° C. in about 30 minutes, where it was maintained within 3°, for an additional 5 hours. The combined residues of three runs weighed 232.1 grams, while a total of 107.5 grams of overhead product was collected.

The overhead condensate was distilled through a 27-plate packed column, and the product distribution is given in Table I. The acid consituents were determined by a consideration of the boiling ranges and neutralization values while the hydrocarbons were identified by extraction of cuts with concentrated sulfuric acid and determination of the refractive index and specific gravity of each paraffin phase. Although 2, 4-dinitrophenylhydrazine reagent gave positive

Table I. Product Distribution in Overhead Condensate

Compound	Weight %
Light hydrocarbons	3.7
Water	51.7
Formic acid	4.5
Acetic acid	1.1
Propionic acid	1.1
Butyric acid	1.0
Octane	0.6
Nonane	4.3
Decane	12.8
Undecane	10.3
Octanal	Trace identified
Total	91.1

Table II. Alcohols Obtained by Reduction of Tricosanone Oxidation Product

Alcohol	Weight %
Heptyl (and lower)	2.2
Octyl	1.5
Nonyl	3.5
Decyl	10.2
Undecyl	18.5
Dodecyl	13.2

indications of carbonyl compounds in each cut, only the *n*-octanal derivative was isolated in sufficient quantity for positive identification by a mixed melting point determination with an authentic sample.

Reduction of Tricosanone Oxidation Product with Lithium Aluminum Hydride. A solution of 100 grams of the tricosanone oxidation product in 200 ml. of ether was added dropwise to a solution of 50 grams of lithium aluminum hydride in 500 ml. of ether over a 4-hour period. The mixture was refluxed for an additional hour, allowed to stand over night, and then hydrolyzed with water. The solution obtained by the addition of excess sulfuric acid was extracted five times with 200-ml. portions of ether which were combined and concentrated to 500 ml. To this solution was added two 40-ml. ether extractions of an aqueous phase which separated during the concentration of the ether solution, and after drying over Drierite for 16 hours, filtration, and removal of the ether, there was obtained 60 grams of an oil having a saponification number of 18, neutralization value of 3.5, and hydroxyl number of 393.

Table III. Analysis of Higher Boiling Cuts Obtained from Reduction of Triconsanone Oxidation Product

							Hydroxyl Content			
							Infrared		Elemental Analysis	
Cut	Boiling Range, Mm.	Refractive Index, n_D^{20}	C	H	M. W.	Formula	Per g.	Per mole	Per g.	Per mole
23	142-3/10	1.4522	73.42	13.08	180	$C_{14.4}H_{31.0}O_2$	6.8×10^{-3}	1.2	8.4×10^{-3}	1.5
26	157-9/10	1.4589	73.06	12.61	207	$C_{13.6}H_{28.2}O_2$	6.2×10^{-3}	1.3	8.9×10^{-3}	1.9
Decanediol	175/13	1.4550	69.00	12.70	174	$C_{10}H_{22}O_2$	...	...	11.5×10^{-3}	2.0

The product was fractionated on a micro Podbielniak spinning band column. After removal of a small amount of ether, cuts boiling up to 160° at 40 mm. were taken, and these represented 49% of the charge. On the basis of boiling point, refractive index, elemental analysis, and molecular weight, the product contained the alcohols listed in Table II.

The higher boiling fraction was analyzed by infrared and elemental analytical techniques. The relatively high ratio of oxygen to carbon, by either method, and the boiling range indicate glycols, hydroyethers, or both in the 10- to 18- carbon range. In Table III the data on the two major high boiling plateaus are presented; literature values on 1,4-decanediol (*5*) are included for comparison.

Examination of spectra of the higher cuts in the infrared region showed no evidence of intrabonded hydroxyl groups —i.e., no glycols in which the hydroxyl groups were on adjacent carbons, or were separated by only one methylene group. By the use of periodate analysis (*11*), it was shown quantitatively that the higher distillation cuts contained no 1, 2-glycols. A qualtitative test on the entire reduction product was negative, indicating that the only dioxygenated molecules present were those which have at least two carbon atoms between the oxygen-containing groups.

Chromatographic Separation of Tricosanone Oxidation Product over Silicic Acid. Into a column 1 inch in diameter was poured a slurry of silicic acid (Mallinckrodt No. 2847, 100 mesh) in hexane. After the column settled to a length of 41 inches a solution of 26.8 grams of the oxidation product in 100 ml. of hexane was added. The chromatogram was developed initially with hexane and, after removing an initial cut of 70 ml., the second cut of 12 ml. was taken which contained the first color to wash through. All subsequent cuts were approximately 12 ml. The following eluotropic series was used: 250 ml. of hexane, 75 ml. of iso-octane, 50 ml. of 1% chloroform in hexane, 51 ml. of 2% chloroform in hexane, 52 ml. of 4% chloroform in hexane, 54 ml. of 8% chloroform in hexane, 60 ml. of 16% chloroform in hexane, 50 ml. of 32% chloroform in hexane, 100 ml. of chloroform, 50-ml. portions of the following percentage concentrations of methanol in chloroform: 1, 2, 4, 10, 25, and 50; and finally 150 ml. of pure methanol. The cuts were isolated by evaporation of solvent, and a consideration of cut *vs.* weight (Figure I) indicated that the product was separated into four main fractions (Table IV).

In Table V are the analytical values obtained on selected major cuts in each fraction. Included for comparison with the most highly oxidized portions are the corresponding data for an aldehyde-acid type product obtained by Zellner (*15*) by the oxidation of paraffin wax to saponification values over 500.

Perhaps the most useful information on the nature of the oxidation product was obtained by the analysis of selected cuts from each fraction for acids, before and after saponification (Table VI). Monobasic acids from octanoic to dodecanoic and dibasic acids from succinic to sebacic were determined by liquid partition chromatography (*6, 12*).

Table IV. Chromatographic Separation of Tricosanone Oxidation Product over Silicic Acid

Fraction	Cuts	Weight, g.	% of Charge
1	1-13	10.50	39.2
2	27-34	1.80	6.7
3	45-62	4.57	17.1
4	64-75	8.89	33.2
			96.2

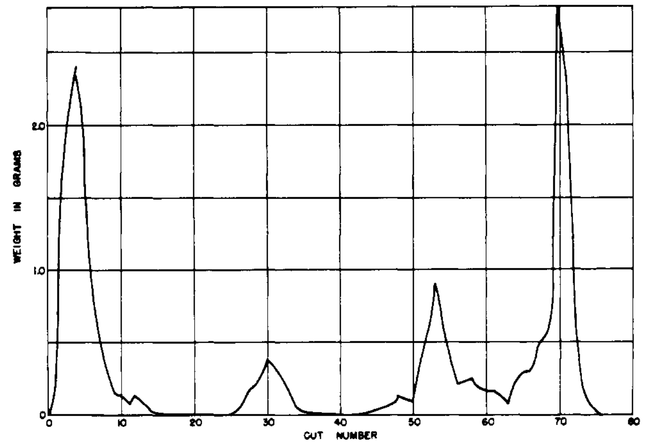


Figure 1. Distribution of products by chromatographic separation

Table V. Analysis of Chromatographic Cuts

Cut and Weight	Carbon, %	Hydrogen, %	Approx. Mol. Wt. (Camphor)	Acid Mg. KOH/G.	Saponification Value, Mg. KOH/G.	Carbonyl, Wt. %
2 1.65	76.7	12.1	330	48	207	0.31
3 2.02	73.0	11.4	237	209	291	0.15
4 2.40	72.1	11.7	234	217	309	0.13
6 1.04	71.0	11.5	238	221	351	0.21
32-30 1.00	71.7	10.9	341	74	312	0.04
53 0.90	70.0	10.3	464	47	354	0.72
68 0.54	67.0	9.4	464	74	396	0.96
71 2.32	58.6	8.1	331	280	560	0.93
72 0.70	63.2	8.8	420	195	476	0.93
Zellner's acid	50.6	6.6	236	470	683	...

The saponification procedure is illustrated by the following example. A solution of 0.1933 grams of combined cuts 28 to 34 in 5 ml. of 1*N* ethanolic (95%) KOH was refluxed for 6 hours and then poured into a small beaker to allow the solvents to evaporate. The oily residue was acidified with 2 ml. of concentrated HCL and then extracted with 5 10-ml. portions of hexane. After removal of the hexane and vacuum drying the product weighed 0.1788 grams (92.5%); it was analyzed for monobasic acids. To check the efficiency of the saponification and extraction steps, and the precision of the chromatographic determination, 0.1482 grams of the same material tagged with 0.0115 grams (7.2%) of palmitic acid was saponified by a different procedure prior to analysis. The material was refluxed with 5 ml. of 2*N* aqueous KOH for 6 hours and then diluted to 30 ml. with distilled water, extracted twice with 15-ml. portions of ehter, cooled to 0° with crushed ice, acidified with dilute hydrochloric acid, and extracted three times with 20-ml. portions of ether. Evaporation of the ether solutions gave 0.0156 grams of neutral material readily soluble in hexane and 0.1480 grams of acidic material. The results are compared in Table VI and VII.

Table VI. Distribution of Monobasic Acids in Chromatographic Cuts

		Carbon Atoms				
		12	11	10	9	8
Fraction	Cut	Free Acids Present, Wt. %				
1	2-3	17.9	16.4	0	0	0
1	3-4	20.3	26.7	16.2	5.8	0
1	7-8	16.2	22.0	12.3	8.9	13.4
2	28-34	0	0	0	0	0
3	54-55	0	0	0	0	0
Total oxidation product		7.1	10.8	3.5	1.8	0.9
		Acids after Sponification				
2	28-34	6.3	8.2	4.2	3.8	...
2	28-34[a]	6.3	8.6	4.6	5.0	3.3
3	54-55	3.7	4.8	1.8	0.9	...
4	70	0	0	0	0	0

[a] Second saponification procedure. Analysis corrected for 7.1% palmitic acid found by analysis.

Table VII. Distribution of Dibasic Acids in Chromatographic Cuts

		Carbon Atoms						
		10	9	8	7	6	5	4
Fraction	Cut	Free Acids Present						
3	54-55	0	0	0	0	0	0	0
4	69	0	0.6	0.8	0.5	0.4	0.5	0
4	72	1.5	1.6	1.6	3.1	5.6	5.8	2.9
Total oxidation product		0.8	0.6	1.2	0.8	0.5	0.3	0
		Acids after Saponification						
3	54-55	0	0	0	0	0	0	0
4	69	0	0.4	0.5	0.2	0.6	0.5	0.2
4	72	2.9	2.5	4.6	10.0	9.1	14.2	7.8

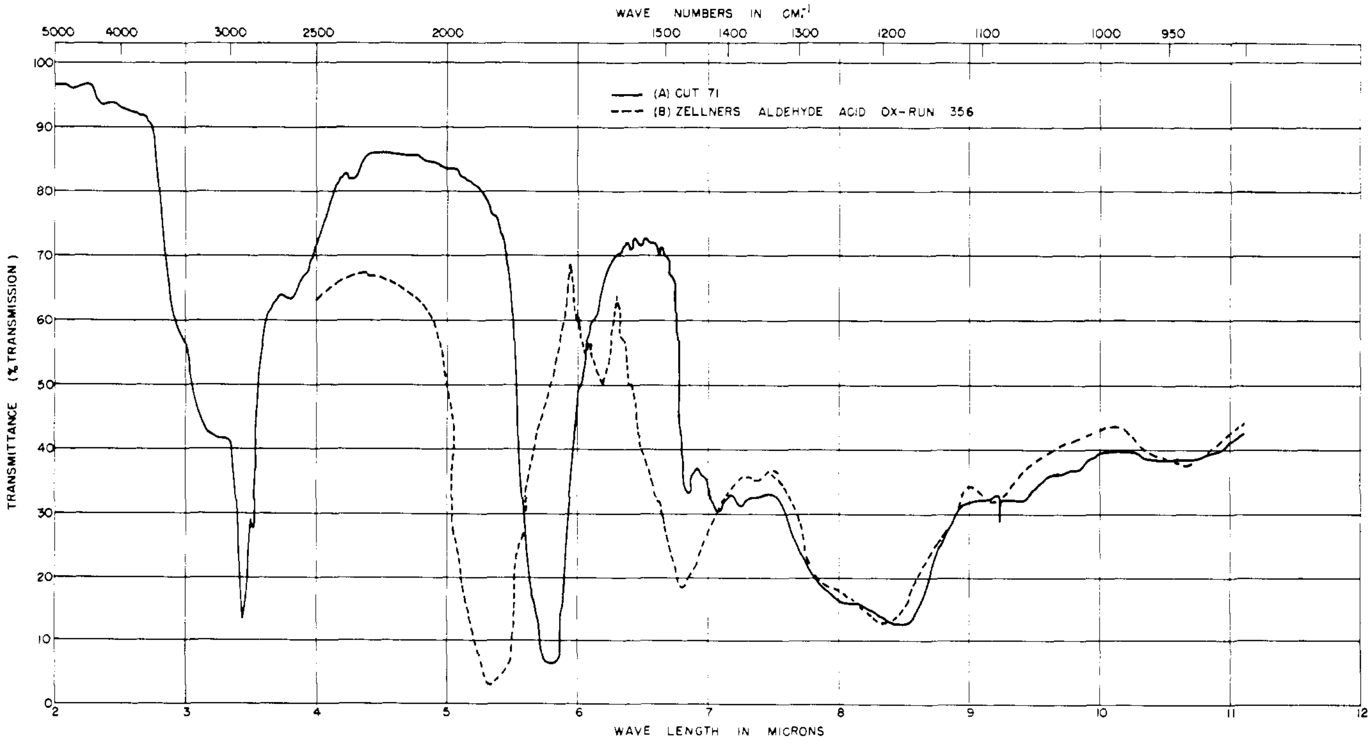


Figure 2. Infrared spectra of highly oxidized products

The chromatographic analysis of the oxidation product over silica gel resulted in an excellent separation into compound types with apparently little holdup, saponification, or degradation. The product was divided into four fractions (Figure 1) which represented increasing degrees of oxidation and complexity. The efficiency of the silicic acid was further shown by the changing nature of the cuts within each fraction. The first fraction (39.2%), in which it was expected to find the least polar products, contained mainly fatty acids. The unreacted tricosanone (about 8% of the bottoms product) was concentrated in the initial cuts, and the acid distribution shifted to the smaller fatty acids with the later cuts. The weight discrepancies and the ester values for cuts in this fraction may be explained by the presence of esters of fatty acids and neutral alcohols.

The presence of hydroxyacids was indicated in the second fraction (6.7%). Saponification showed that it consisted of 10% neutral material and about 90% total acids, of which 27.8% were fatty acids. Because the unsaponified material contained no free fatty acids and no free or esterified dibasic acids, this portion of the oxidation product probably consisted of hydroxyacids and fatty acid esters of hydroxyacids.

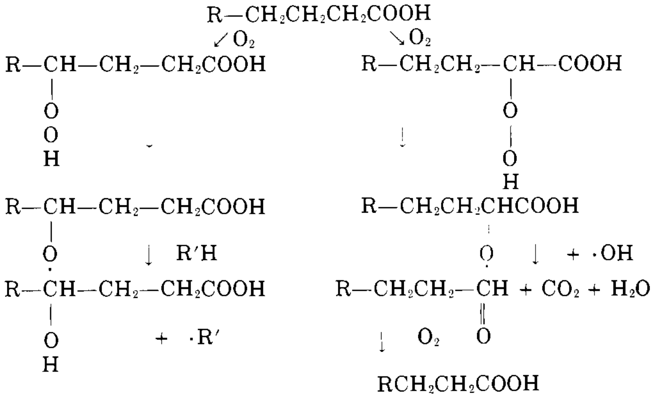
The third fraction (17.1%) was qualitatively similar to the second but contained less (11%) esterified fatty acids, a higher molecular weight, saponification value and oxygen content, and a lower acid value. This would appear to be hydroxyacids polymerized to a greater extent than the second fraction, perhaps containing three or four units per molecule.

The fourth fraction (33.2%) contained the most highly oxidized material, and contained substantial amounts of free and esterified dibasic acids. It had been thought originally that this most highly oxygenated portion might be the same as Zellner's water soluble difunctional aldehyde-acid oxidation product (*15*). However, a comparison of the infrared spectra (Figure 2) showed it to have a different composition although it was also a complex acid-ester mixture. The cuts in fraction 4 contained methyl groups (7.2mμ), which Zellner's material did not, and had no absorption at 3.8mμ, indicating the absence of free aldehyde groups. Furthermore, the cuts obtained here had higher molecular weights and carbon and hydrogen content, and lower acid and saponification values and oxygen content than Zellner's material (Table V). From the available data it is concluded that this fraction consists mainly of dibasic acids and esters of dibasic acids with hydroxyacids. Other compound types such as ketoacids, hydroxyketones, and esterification and condensation products of these are probably present.

DISCUSSION

The autoxidation of a ketone proceeds via attack at the methylene groups adjacent to the carbonyl (*10*). In the case of normal paraffin oxdiation, although there is preferential attack at the methylene groups adjacent to terminal methyl groups at very low energy levels (*7*), random attack at all methylene groups in the chain occurs at the temperatures of paraffin oxidations carried out in practice (*1*). Earlier authors have shown that both base- and acid-catalyzed ketone oxidations proceed via an α-ketoperoxide which decomposes into an aldehyde, from the peroxide portion, and an acid, from the keto portion. Unless the aldehyde is removed from the reaction site, it is further oxidized to an acid. Although it is not feasible to rule out the possibility that some initial attack on the long alkyl chains of tricosanone occured at positions away from the carbonyl group, the isolation of large amounts of lauric and undecanoic acid indicates that attack predominates at the α-methylene groups as is the case with smaller ketones. Secondary attack appears to give products similar to general paraffin (*13*) or fatty acid (*9*) air oxidation. It was shown by the acid distribution and the distribution of alcohols obtained by the reduction, that the oxidation product contained more 11-carbon chains than 12-carbon chains. This would indicate that, while the distribution of dibasic acids shows that extensive oxidation of the fatty acids occurs along the entire chain, the favored position of attack, as with the ketones, is again at the α position. Thus, one possible explanation for the high concentration of the 11-carbon acid is that while the undecanoic acid is being oxidized to decanoic acid it is also being formed by the same type of oxidation of dodecanoic acid and should be present in greater amounts than the 12-carbon acid. In addition, the material blown overhead during the oxidation contained more decane than undecane. This indicated that the hydrocarbons are formed by the thermal decarboxylation of the acids and thus further indicates the greater concentration of 11-carbon acid.

Attack occurs at all positions on the chain and, in addition to oxidation at the α position, a considerable amount of attack occurs on the β carbon as well as more distant positions, although no evidence for 1, 2- or 1, 3- dioxygenated compounds was found, particularly by examination of the reduction products. This may be explained by considering the hydroperoxide intermediate which is generally considered to lead to an oxy free radical. Such a free radical in general undergoes either chain cleavage or hydrogen abstraction to form a hydroxyl group; when the oxy free radical is in the α or β position to a carboxyl group, the electron-withdrawing power of the carboxyl group causes cleavage to occur predominantly.



However, only attack at the gamma position and those further removed leads to difunctional products.

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