bilizer) increases with increasing soap concentration are characterized by an increase in long X-ray spacings to the point at which the system becomes saturated with the compound being solubilized. Hydrocarbons such as benzene, ethyl benzene, and normal paraffins fall into this class. Another type is that in which the MR remains constant above the concentration where the soap assumes its full colloidal properties, and this is characterized by no change in long X-ray spacing. Examples of this type are soap-soap, soap-fatty acid, soap-alcohol, and possibly as a subtype, soap-dye systems. These systems are shown to be mixed micelles in which the solubilized compound is oriented with the long axis of the solubilized compound lying approximately parallel and in the plane of the long axis of the soap molecules, the hydrophylic group of both constituents being toward the water interface. Protein-detergent complexes are discussed from the point of view of solubilization.

REFERENCES

1. W. Heller and H. B. Klevens, J. Chem. Phys. *14*, 567 (1946).
2. G. S. Hartley, J. Chem. Soc. *1938*, 1968.
3. J. W. McBain and J. J. O'Connor, J. Am. Chem. Soc. *63*, 875 (1941).
4. H. B. Klevens, unpublished data.
5. J. W. McBain and A. A. Green, J. Am. Chem. Soc. *68*, 1731 (1946).
6. J. W. McBain, R. C. Merrill, Jr., and J. R. Vinograd, J. Am. Chem. Soc. *63*, 670 (1941).
7. H. V. Tartar and R. D. Cadle, J. Phys. Chem. *43*, 1173 (1939).
8. L. Shedlovsky, G. D. Miles, and G. V. Scott, J. Phys. Colloid Chem. *51*, 391 (1947).
9. I. M. Kolthoff and W. Stricks, J. Phys. Colloid Chem. *52*, 915 (1948).
10. W. Heller and H. B. Klevens, High Polymer Forum, Am. Chem. Soc. Meeting. Chicago, Illinois, Sept. 9-13, 1946.
11. P. A. Thiessen and R. Spychalski, Z. physik. Chem. *156A*, 435 (1931).
12. K. Hess and J. Gundermann, Ber. *70B*. 1800 (1937).
13. J. Stauff, Kolloid Z. *89*, 224 (1939); *96*, 244 (1941).
14. H. Kiessig and W. Philippoff, Naturwissenschaften *27*, 593 (1939).
15. H. Kiessig, Kolloid Z. *96*, 252 (1941); *98*, 213 (1942).
16. W. Philippoff, Kolloid Z. *96*, 255 (1941).
17. S. Ross, J. Phys. Chem. *46*, 414 (1942).
18. E. W. Hughes, W. M. Sawyer, and J. R. Vinograd, J. Chem. Phys. *13*, 131 (1945).
19. W. D. Harkins, R. W. Mattoon, and M. L. Corrin, J. Colloid Sci. *1*. 108 (1946).
20. R. W. Mattoon, R. S. Stearns, and W. D. Harkins, J. Chem. Phys. *16*, 644 (1948).
21. G. S. Hartley, "Aqueous Solutions of Paraffin-Chain Salts," Hermann et Cie, Paris, 1936,
22. H. B. Klevens, Colloid Symposium, Am. Chem. Soc., Cambridge, Mass., June 23-25, 1948.
23. W. D. Harkins, R. W. Mattoon, and M. L. Corrin, J. Am. Chem. Soc. *68*, 220 (1946).
24. M. J. Buerger, Am. Mineralogist *30*, 551 (1945).
25. H. B. Klevens, J. Chem. Phys. *14*, 742 (1946); J. Phys. Colloid Chem. *52*, 130 (1947).
26. W. D. Harkins, R. W. Mattoon, and R. Mittlemann, J. Chem. Phys. *15*, 763 (1947).
27. J. W. McBain and H. McHan, Colloid Division, Am. Chem. Soc., New York, Sept. 15-19, 1947.
28. H. B. Klevens, J. Phys. Colloid Chem. *51*, 1143 (1947); J. Colloid Sci. *2*, 365 (1947).
29. H. B. Klevens, "Effect of Structure on Critical Micelle Concentration, III," in preparation.
30. I. M. Kolthoff and W. E. Harris, J. Polymer Sci. *2*, 49 (1947); *2*, 72 (1947).
31. W. D. Harkins, J. Am. Chem. Soc. *69*, 1428 (1947).
32. E. I. Valko, Ann. N. Y. Acad. Sci. *45*, 451 (1946).
33. H. P. Lundgren, D. W. Elam, R. A. O'Connell, J. Biol. Chem. *149*, 183 (1943).
34. F. W. Putnam and H. Neurath, J. Am. Chem. Soc. *66*, 692 (1944); J. Biol. Chem. *159*, 195 (1945).
35. H. B. Bull, J. Am. Chem. Soc. *67*, 10 (1945).
36. M. L. Anson, J. Gen. Physiol. *23*, 233 (1939).
37. F. W. Putnam, Advances in Protein Chemistry *4*, 79 (1948).
38. J. F. Foster, Colloid Symposium, Am. Chem. Soc., Cambridge, Mass., June 23-25, 1948.

Factors Which Affect the Stability of Highly Unsaturated Fatty Acids.[1] II. The Autoxidation of Linoleic and Alkali Conjugated Acid in the Presence of Metallic Naphthenates[2]

A. H. JACKSON [3] and F. A. KUMMEROW, Kansas Agricultural Experiment Station,[4]
Manhattan, Kansas

DRIERS have been in commercial use for some time, yet no concise mechanism has been advanced as to their role in olefin oxidation. Riemenschneider (1) suggested that they may function by increasing the efficiency of energy transfer from one molecule to another. Furthermore, Nicholson (2) has shown that it is the concentration of drier cation that determines the catalytic activity. The activity was not destroyed by adsorption (3) or by saturating coordination valence of the drier (4).

In addition to listing the relation of driers to polymerization and gelation, Elm (5) stated that the metal portion oscillated between two stages allowing it to activate the atmospheric oxygen and pass it on to a drying oil molecule. A "reducing inhibitor" destroying action (6) and an initial peroxide stabilizing role (5) have been suggested. Gardner and Waddell (7) believed that driers form a series of unstable complexes with several of the products and reactants produced during autoxidation, polymerization, and gelation. It is now generally believed that driers function as promoters, or as pseudo rather than true catalysts.

A plausible chemical mechanism for drier action during the autoxidation of tetralin has been postulated. Yamada (8) has shown that Mn, Co, and Pb compounds raise the decomposition reaction order of tetralin hydroperoxide one step, that is from the first to the second order. Ivanov *et al.* (9) and Medvedev (10) have demonstrated a similar role for the transition metals in hydrocarbon autoxidation.

Robertson and Waters (11) have classified metallic salts as "secondary catalysts" and have pointed out why it is of no particular advantage to increase the concentration of the promoters above a certain value.

In this laboratory we have been concerned with the factors affecting the stability of highly unsaturated fatty acids (12, 13). A study of the autoxidation of linoleic and alkali conjugated linoleic acid was presented in another paper (14). The modifica-

---

[1] The subject matter of this paper has been undertaken in cooperation with the Office of Naval Research. The opinions or conclusions contained in this report are those of the authors. They are not to be construed as necessarily reflecting the views or indorsement of the Navy Department.

[2] Portion of a thesis presented by A. H. Jackson as partial fulfillment of the requirements for the degree of Master of Science in Chemistry at Kansas State College.

[3] Present address: Department of Biochemistry, Meharry Medical College, Nashville, Tennessee.

[4] Contribution No. 367, Department of Chemistry, Kansas State College.

TABLE I

The relation of peroxide content to enolizable products of autoxidation

Time in hours	Unconjugated linoleic acid			Unconjugated linoleic acid + co-naphthenate			10,12-linoleic acid			10,12-linoleic acid + co-naphthenate		
	P.V.[1]	aV[2]	KOH[3] aV	P.V.	aV	KOH aV	P.V.	aV	KOH aV	P.V.	aV	KOH aV
1.0	331	0.183	0.756	240	1.025	0.765	44	0.000	0.000	10	0.357	0.000
2.0	636	0.307	2.365	102	1.266	1.350	66	0.000	0.000	9	0.150	0.000
4.0	756	1.022	1.930	117	1.830	3.820	96	0.851	0.000	12	0.705	0.000
8.0	589	1.560	0.865	81	1.722	1.215	153	0.652	0.326	17	0.577	0.660
13.0	538	1.575	2.560	81	1.472	2.720	243	0.573	1.890	33	0.584	1.850
20.0	450	1.131	2.720	85	1.088	2.680	305	0.391	1.640	59	0.693	1.700
29.0	399	0.882	2.265	47	1.172	2.845	91	0.536	2.160	47	0.956	2.180

[1] Peroxide value.
[2] Absorption value at 2770 Å.
[3] Absorption value at 2770Å 48 hours after adding 5% alcoholic KOH.

tions brought about by the addition of naphthenate[5] driers are presented here.

Experimental

Preparation of Materials. The linoleic acid was prepared from corn oil[6] by the method of Rollett (15). The free acid was subjected to distillation at 100 mμ. and 150°C. The colorless distillate had an iodine value of 180, a peroxide number of zero, and a specific absorption coefficient of 0.3 at 2320 Å.

The alkali conjugated linoleic acid was prepared from linoleic acid by the method of Holman and Elmer (16). It had a specific absorption coefficient of 86.0 at 2320 Å. The 10,12-linoleic acid was prepared from the distilled methyl esters of dehydrated castor oil[7] according to the method of Von Mikusch (17). This material was purified by repeated fractional crystallization from Skellysolve F, ethyl alcohol, and diethyl ether. The final product had a melting point of 55-56°C. and a specific absorption coefficient of 112.0 at 2320 Å. It was preserved by suspension in ethyl alcohol at —22°C. The white crystals of the 10,12-linoleic acid were filtered from the solution as needed.

Oxidation Procedure. The oxidations were conducted by bubbling tank oxygen through heated samples for various known periods of time as described by Allen, Jackson, and Kummerow (14). Five to six mg. of naphthenate drier were accurately weighed into a clean six-inch Pyrex tube and the weight of added sample adjusted to give a catalyst concentration of 0.1%. The oxygen was introduced

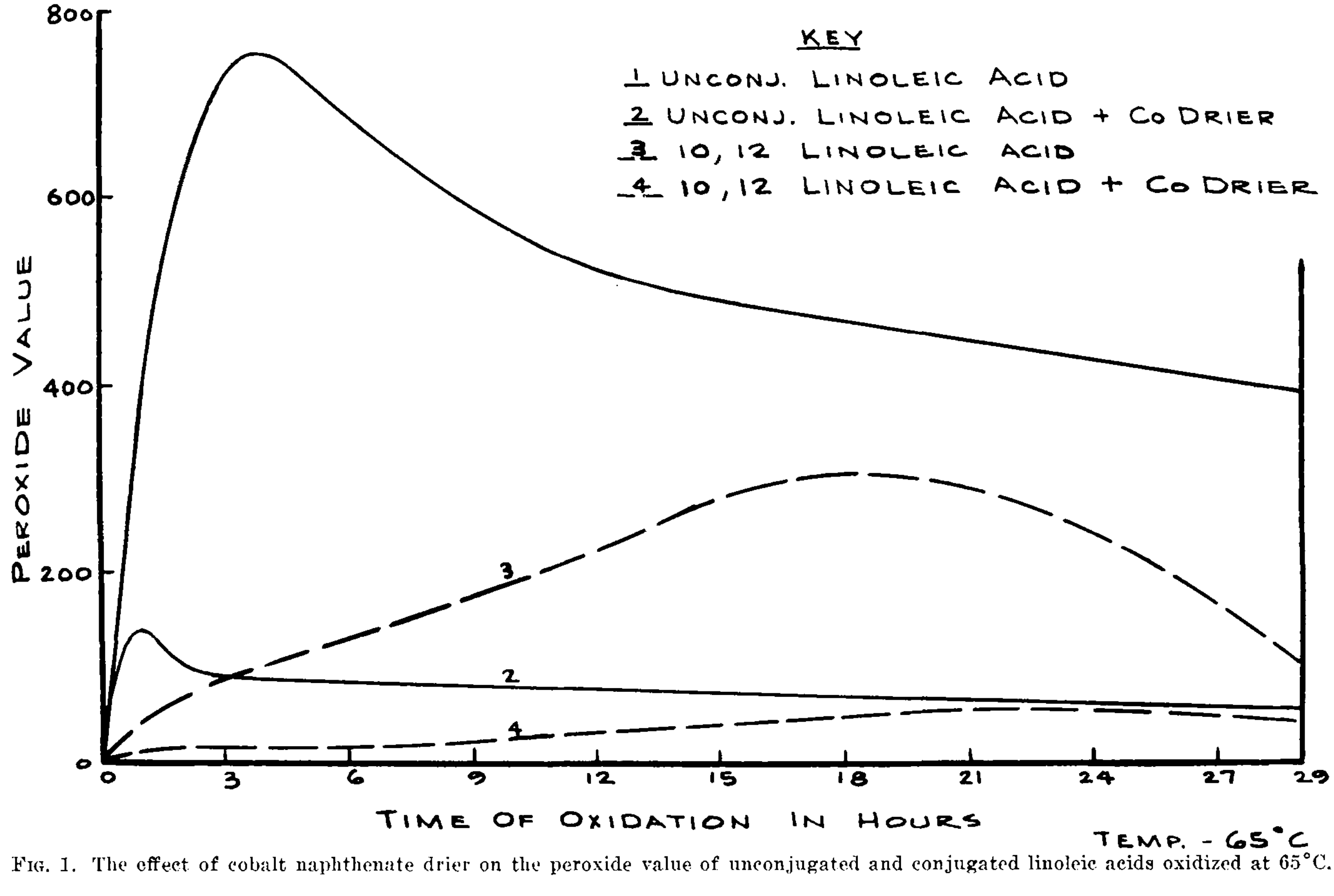

FIG. 1. The effect of cobalt naphthenate drier on the peroxide value of unconjugated and conjugated linoleic acids oxidized at 65°C.

---

[5] Naphthenate driers obtained through the courtesy of S. B. Elliott, Ferro Chemical Corporation, Cleveland 14, Ohio.

[6] A degummed oil furnished through the courtesy of Corn Products Refining Company, Argo, Illinois.

[7] G. H. Dehydrated Castor Oil obtained through the courtesy of O. Eisenschmil, The Scientific Oil Compounding Company, Chicago, Illinois.

into the samples through glass inlet tips. These tips led into clamped tubes suspended in a 12" by 12" insulated Pyrex jar which contained light mineral oil. The temperature was regulated to a constancy of ±0.5°C. by an Aminco thermostatically controlled heating unit. At appropriate intervals approximately 0.3-g. samples were removed for peroxide (18) and spectrophotometric absorption measurements (19,20). The latter were determined with a 100-mg. sample diluted to 100 ml. with purified ethyl alcohol and read on a Beckman Spectrophotometer at 2340 Å. The peroxide values were determined on 100 mg. of the sample which was weighed into a 125-ml. ground glass flask, 5 ml. of chloroform, acetic acid (3:1) added and titrated immediately with N/100 sodium thiosulfate. A sample without drier was run along with each group of catalized samples.

Results

The addition of naphthenate driers to either conjugated or unconjugated linoleic acid decreased the observed peroxide value during autoxidation (Fig. 1). Driers seemed to reduce the amount of peroxide oxygen most effectively when added to unconjugated acid. After the third hour of oxidation the unconjugated acid actually contained less peroxide oxygen than the 10,12-linoleic acid to which no drier had been added. However the amount of peroxide oxygen formed was also dependent on the temperature at which the autoxidation was carried out. The maximum amount of peroxides formed during the autoxidation of the unconjugated acid was larger at 30°C. than at 65°C. (Fig. 2). On the other hand, the conjugated acid contained approximately the same maximum amount of peroxides at 30° or 65°C.

The addition of driers to either conjugated or unconjugated linoleic acid also had a pronounced effect on diene conjugation. This fact was more noticeable in the samples which had been oxidized at 30°C. (Fig. 3) than in those which had been oxidized at 65°C. (Fig. 4). At 30°C. the specific absorption coefficient of the unconjugated acid increased more rapidly and of the conjugated acid decreased more rapidly in the presence of drier. The extent of diene conjugation seemed to parallel peroxide formation but declined earlier.

The effect of naphthenate driers on the amount of peroxide oxygen formed (Fig. 5), and the extent of diene conjugation (Fig. 6) seemed to depend on the cation present. Cobalt had the most pronounced and zinc the least effect. In another run cobalt and manganese had the most pronounced effect and calcium and zinc the least effect.

Discussion

These results indicate that driers promote more rapid "drying" through their effect on the rate of

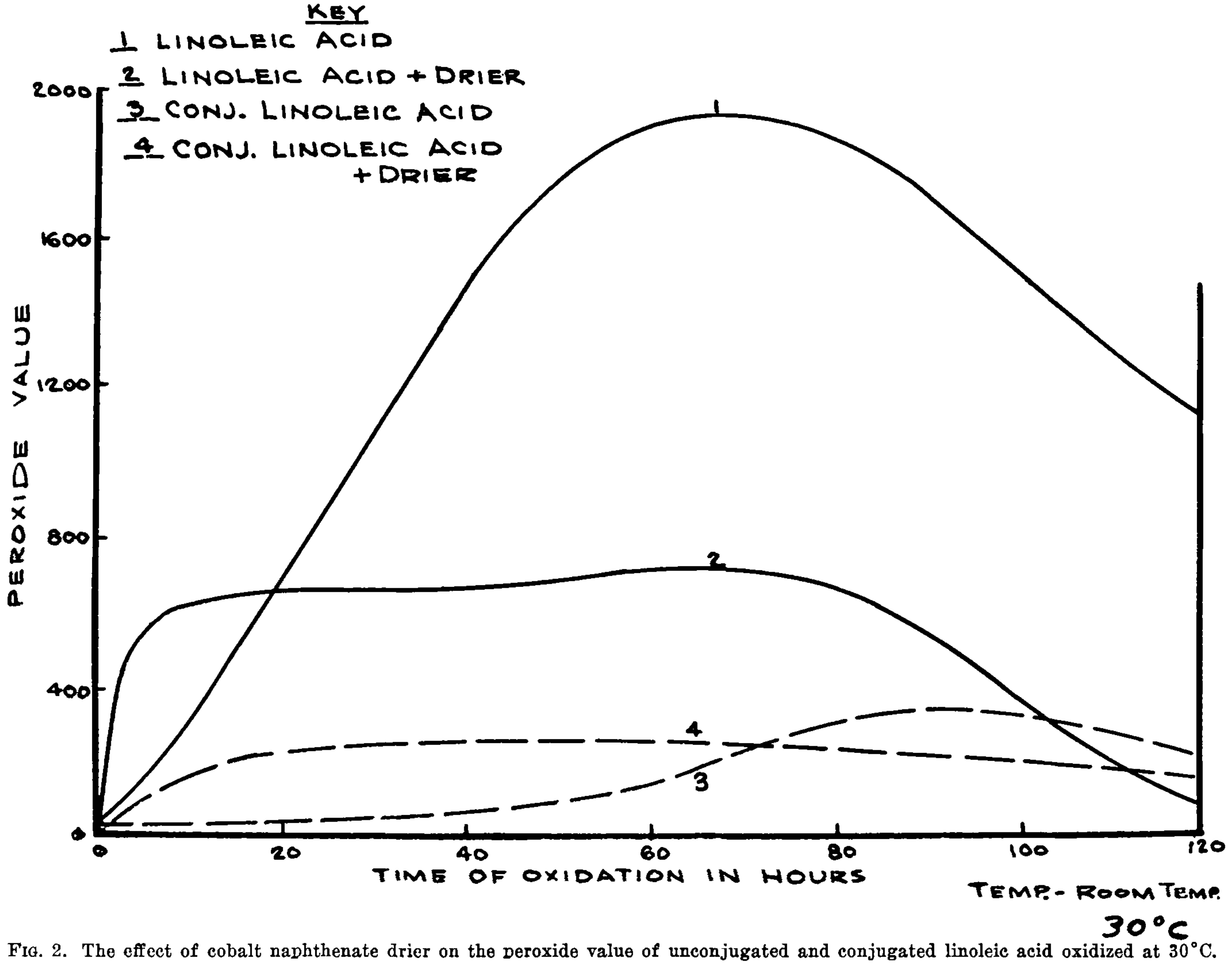

FIG. 2. The effect of cobalt naphthenate drier on the peroxide value of unconjugated and conjugated linoleic acid oxidized at 30°C.

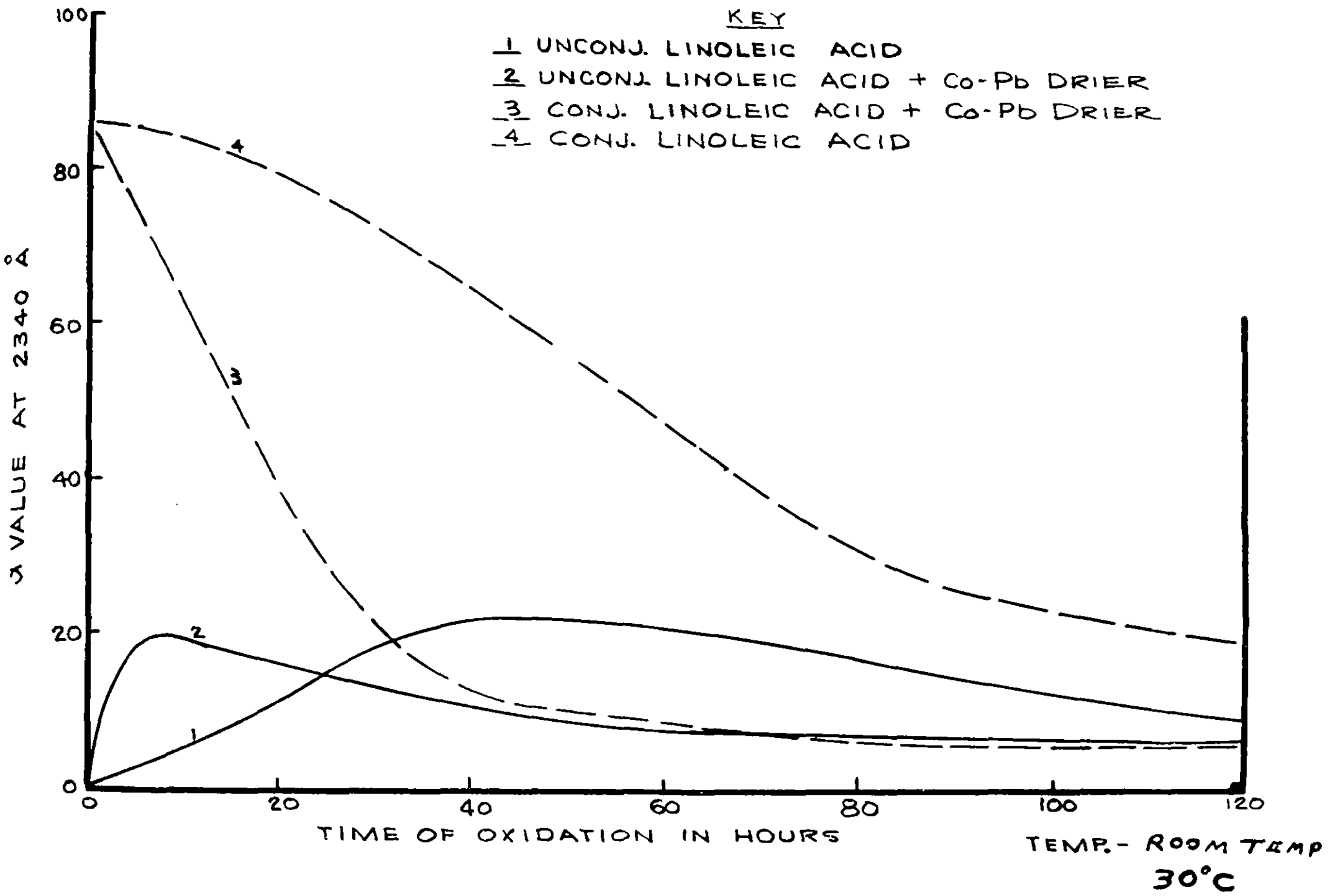

FIG. 3. The effect of cobalt naphthenate drier on the specific absorption coefficient of unconjugated and conjugated linoleic acid oxidized at 30°C.

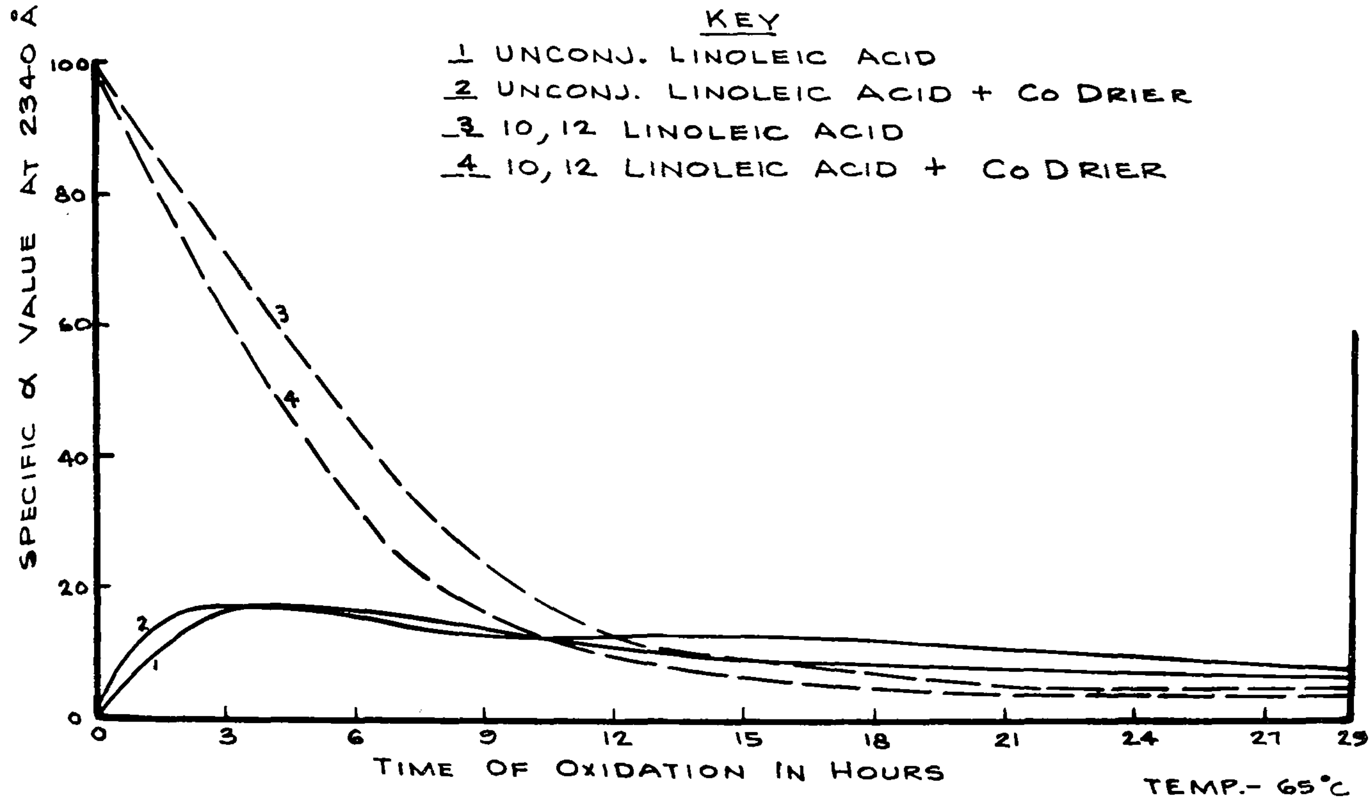

FIG. 4. The effect of cobalt naphthenate drier on the specific absorption coefficient of unconjugated and conjugated linoleic acid oxidized at 65°C.

peroxide formation and the rate of polymerization. Furthermore, the detectable amount of peroxide oxygen increased more rapidly when driers were present. However, the total amount of peroxide oxygen formed was less than in the absence of driers, and therefore the chances of hydroxy and keto acids appearing in the polymerized product are decreased.

In a previous study (14) all of the oxygen was found to be present as peroxide oxygen up to the point at which approximately 0.2 of a mole of oxygen had been absorbed. According to Bolland and Koch (21), all of this peroxide oxygen is present in the form of hydroperoxide. Unfortunately, in the present studies the total amount of oxygen absorbed during autoxidation was not determined. Previous workers (22), however, have noted that the total amount of oxygen taken up was less in the presence of driers.

It seems possible that the activity of driers may be due to an initiation of oxidation chains, or to their decomposition of peroxide, thereby promoting secondary oxidation reactions. Robertson and Waters (11) stated that in the autoxidation of tetralin the metallic salts promoted hydroperoxide decomposition and increased the concentration of the free *OH radical. An electronic balance set up between peroxide and metallic cation was represented as:

$$\mathrm{M^{+} + R{-}OOH \longrightarrow M^{++} + RO{:}^{-} + .OH}$$
$$\mathrm{M^{++} + R{-}O{-}O{:}^{-} \longrightarrow R{-}O{-}O. + Mn^{\cdot}}$$

Whether the above mechanism adequately represents the way in which driers function during the autoxidation of open chain olefins is still questionable. In the present studies the alkali enolization of drier-catalyzed samples did not indicate as large an amount of ketone formation as would be expected if the hydroperoxide of linoleic acid decomposes exactly as that of tetralin, viz., to form a ketone and free *OH. This failure to detect a large amount of ketone may support Farmer's (23) view that olefin $-\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{O{-}OH}$ decomposes to give $-\overset{|}{\underset{|}{\mathrm{C}}}{}^{*}$ *OH and active O.

It also seems possible that driers may be capable of effecting dissociation of a hydrogen atom or a proton as suggested by Hilditch (24) for the action of alkali hydroxide on an unconjugated acid. If the fatty acid molecule minus hydrogen is considered a free radical, the rate of free radical formation would be increased in the presence of driers and the possibility of carbon to carbon polymerization enhanced. The fact that the specific absorption coefficient decreased more rapidly when the 10,12-linoleic acid was subjected to autoxidation in the presence of driers seems to agree with this hypothesis.

The ability of metallic driers to stimulate the formation of conjugated bonds in 9-12-linoleic acid might be useful as a means of classifying paint driers. According to the present results, cobalt and manganese were most effective and calcium and zinc least effective in stimulating conjugation. This effect on the rate of conjugation parallels the effectiveness of these metals as paint driers (22).

Summary

The addition of commercial paint driers to unconjugated linoleic acid increased the rate of diene conjugation during autoxidation and greatly lowered the amount of detectable peroxides. On the other hand, the addition of driers to the conjugated isomer lowered the amount of detectable peroxide but mildly promoted destruction of diene conjugation. The hydroperoxide decomposition role of driers is further

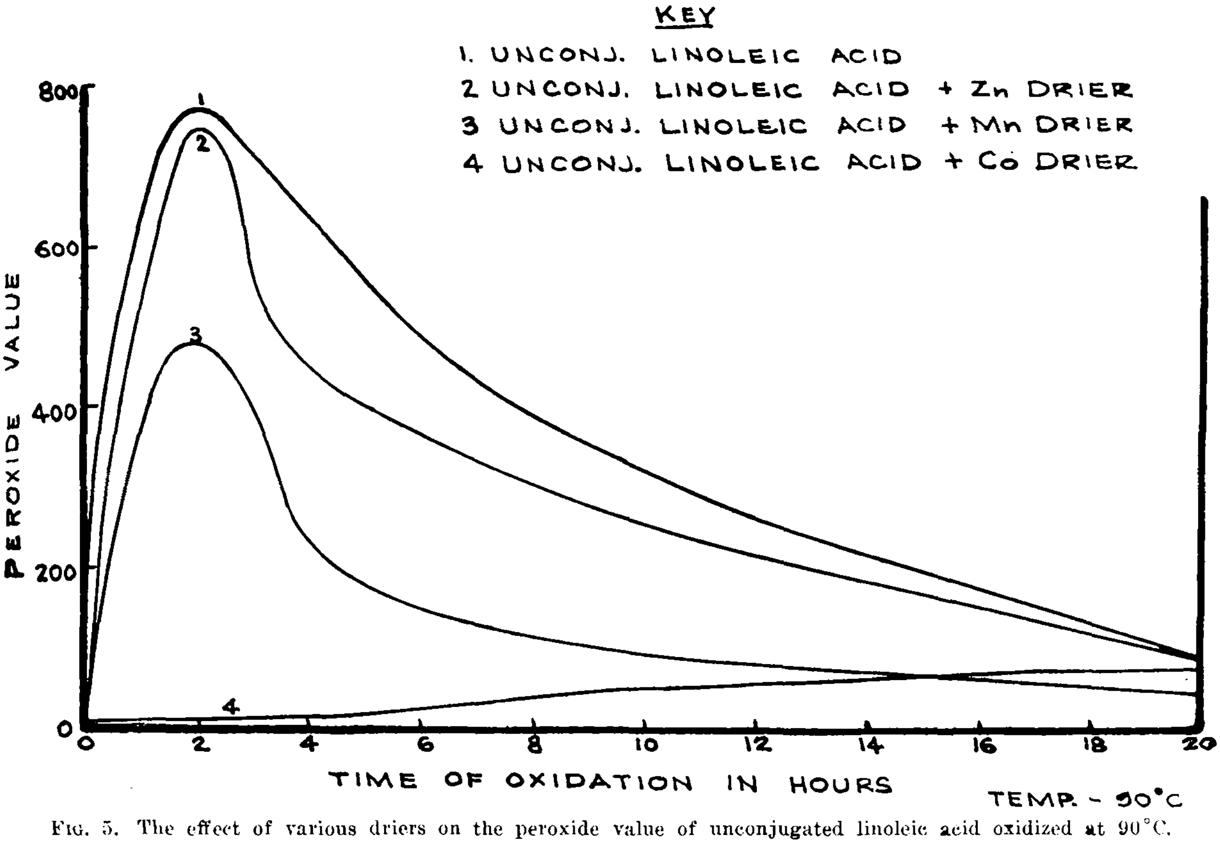

FIG. 5. The effect of various driers on the peroxide value of unconjugated linoleic acid oxidized at 90°C.

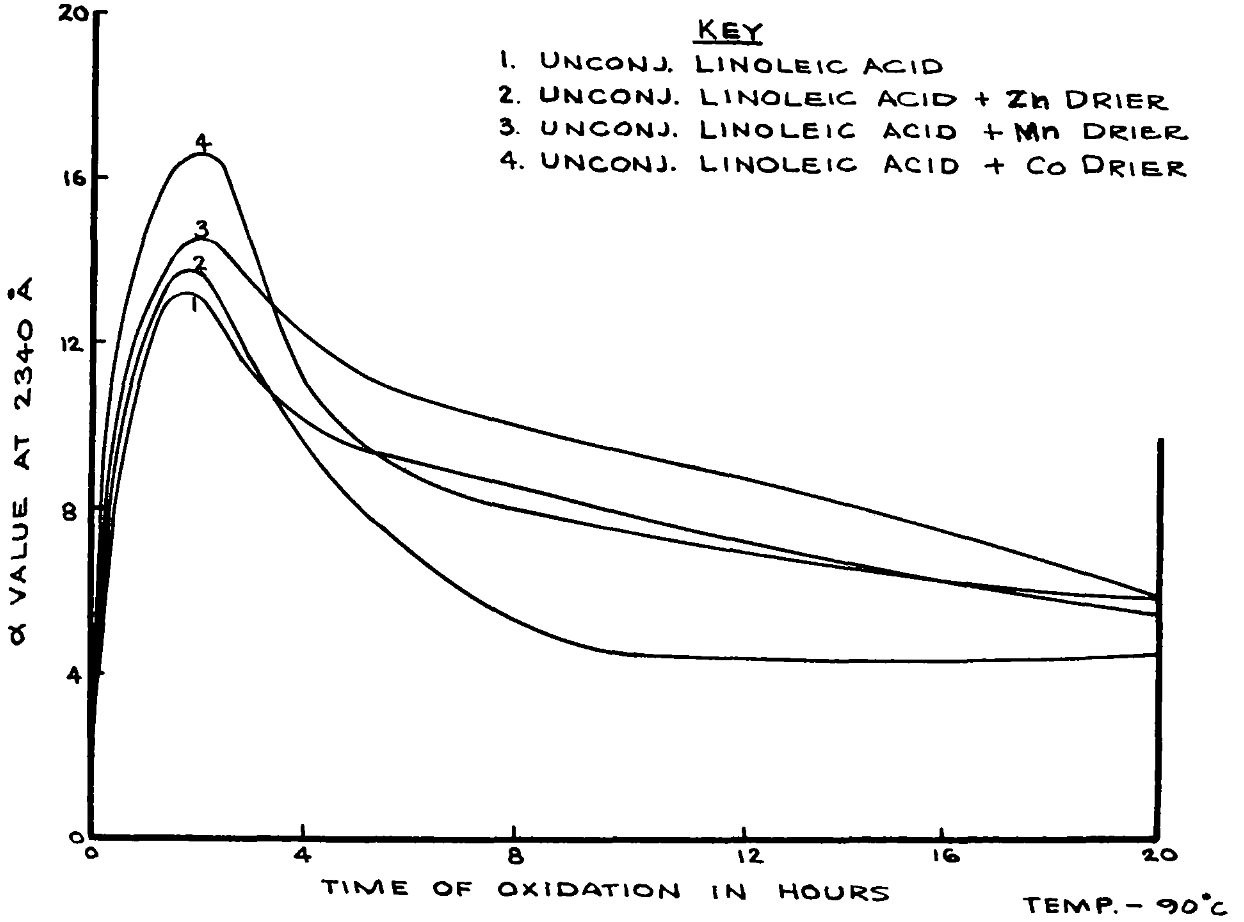

FIG. 6. The effect of various driers on the specific absorption coefficient of unconjugated linoleic acid oxidized at 90°C.

supported. Metallic naphthenates increased the quantity of diene ketones in both unconjugated and conjugated acid though after a longer period of time in the latter case.

Acknowledgment

The authors wish to express their appreciation to Margaret Seaton and Donald Beeson for their aid in carrying out the analytical work involved.

REFERENCES

1. Riemenschneider, R. W., Trans. Am. Assoc. Cereal Chem., *5*, 50 (1947).

2. Nicholson, D. G., and Holley, C. E., Ind. and Eng. Chem., *30*, 114 (1938).

3. Nicholson, D. G., Ind. and Eng. Chem., *31*, 1300 (1939).

4. Nicholson, D. G., Ind. and Eng. Chem., *34*, 1175 (1942).

5. Elm, A. C., Ind. and Eng. Chem., *26*, 386 (1934).

6. Stephens, H., Ind. and Eng. Chem., *24*, 918 (1932).

7. Gardner, W. H., and Waddell, R. B., Ind. and Eng. Chem., *33*, 629 (1941).

8. Yamada, T., Researches Electrotech. Lab. (Tokyo) *443*, 1-2 (1940).; Chem. Zentr., *1*, 3494 (1941); Chem. Abstracts, *38*, 2258 (1944).

9. Ivanov, K. I., Savinova, V. K., and Mikhailova, E. G., Physic. Chem. Jour. U.S.S.R., *12*, 719 (1939).

10. Medvedev, S. S., Acta Physicochim U.S.S.R., *9*, 395 (1938).

11. Robertson, A., and Waters, W. A., Trans. Faraday Soc., *42*, 201 (1946).

12. Kummerow, F. A., and Green, E., J. Am. Oil Chemists' Soc., *24*, 196 (1947).

13. Kummerow, F. A., Hite, J., and Kloxin, S., Poultry Sci., *27*, 689 (1948).

14. Allen, R. R., Jackson, A., and Kummerow, F. A., J. Am. Oil Chem. Soc. (in press).

15. Rollet, A., Z. Physiol. Chem., *62*, 410 (1909).

16. Holman, R. T., and Elmer, O. C., J. Am. Oil Chem. Soc., *24*, 127 (1946).

17. Von Mikusch, J. D., J. Am. Chem. Soc., *64*. 1580 (1942).

18. Wheeler, D. H., Oil and Soap, *9*. 89 (1932).

19. Mitchell, J. H., Kraybill, H. R., and Zscheile, F. P., Ind. Eng. Chem. Anal. Ed., *15*, 1 (1943).

20. Lundberg, W. O., and Chipault, J. R., J. Am. Chem. Soc., *69*, 833 (1947).

21. Bolland, J. L., and Koch, H. P., Jour. Chem. Soc., *445* (1945).

22. Mattiello, J. J., Protective and Decorative Coatings, Vol. I. John Wiley and Sons Inc. (1941).

23. Farmer, E. H., Trans. Faraday Soc., *42*, 228 (1946).

24. Hilditch, T. P., Jour. Oil and Colour Chem. Assoc., *30*, 1 (1947).