# Technical

# Effect of Sugars and Sugar Alcohols on Autoxidation of Safflower Oil in Emulsions[1]

R.J. SIMS, J.A. FIORITI, and J. TRUMBETAS, Technical Center,
General Foods Corp., White Plains, NY 10625

## ABSTRACT

Oxygen absorption rates were measured on liquid emulsions containing safflower oil and glycerol, sugars or sugar alcohols. Stability to oxidation improved as the level of added compound was increased. Emulsion viscosities were higher, and resistance to creaming was better at the higher concentrations of additives. It is suggested that diffusion of oxygen through the oil-water interface is the rate determining step which is probably slower at high viscosity and in the absence of creaming. Freeze-dried emulsions containing safflower oil, protein, polyols and anionic surfactant oxidized more rapidly than did those samples in which either polyol or surfactant was omitted. The differences in oxidation rate could be accounted for on the basis of degree of oil dispersion and porosity of the dried particles. No evidence has been found for any true antioxidant or pro-oxidant effect of these compounds.

## INTRODUCTION

There is conflicting information in the literature concerning the effect of sugars on the autoxidation of fats. Ribose, ribitol and D-2-deoxyribose were found to inhibit peroxidation of methyl linoleate (1), but, in liquid emulsion systems, ribose and other monosaccharides were shown to be rather strong proxidants for this ester (2). Alcohols such as glycerol, xylitol, sorbitol, and maltitol increased the stability of lard in biscuits, but only xylitol functioned with linoleic acid (3). Browing reactions are known to generate pigments which have some antioxidant activity, but recently it was reported that most of this activity is developed at early stages of heating so that the effective stabilizers may actually be colorless (4). This observation has been confirmed in our laboratory. Oxidation rates in the presence of reducing disaccharides such as maltose, lactose or cellobiose were more rapid than in the presence of nonreducing disaccharides such as sucrose (2).

The objective of our work was to determine the behavior of common sugars and sugar alcohols toward a polyunsaturated oil in emulsion systems. Safflower oil was selected as typical of an oil which is difficult to stabilize. The compounds tested included sucrose, dextrose, glycerol and sorbitol. In order to avoid heat and the possibility of complications from browning reactions, storage stability tests were carried out at room temperature. Anionic surfactants were selected which gave prolonged stability to creaming and phase separation in the liquid emulsions so that it was possible to follow the progress of oxidation over a period of several weeks (5). Some preliminary work was also carried out on freeze-dried emulsion systems.

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## EXPERIMENTAL PROCEDURES

### Materials

Refined safflower oil was obtained from the Pacific Vegetable Oil Co., San Francisco, CA. This oil contained no added antioxidants. Sodium stearoyl-2-lactylate (Emplex) was from Patco Products Co., Kansas City, MO. Succinoylated Monoglycerides (SMG) were obtained from Eastman Chemical Products, Inc., Kingsport, TN. Sodium caseinate was a product of the New Zealand Dairy Board. Promine D was produced by Central Soya, Chicago, IL. Sucrose, dextrose monohydrate, sorbitol, and glycerol were all from J.T. Baker, Phillipsburg, NJ.

### Methods

Wet emulsions were prepared by dissolving sugar or sugar alcohol in distilled water, dispersing anionic surfactant and adjusting pH where indicated with 0.1 N NaOH. Oil was added and the mixture was homogenized for 3 min using a Tekmar Probe at maximum speed (Model SD45N from

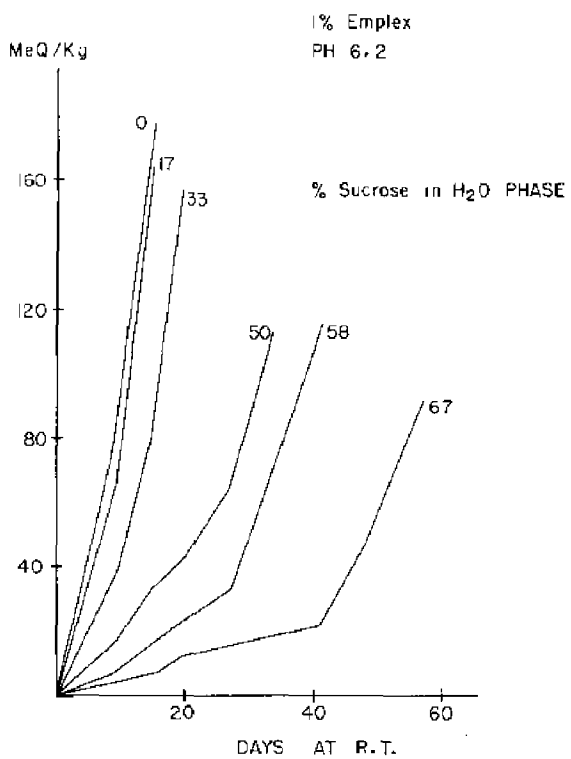


FIG. 1. Oxygen absorption of safflower oil in liquid emulsions containing sucrose.

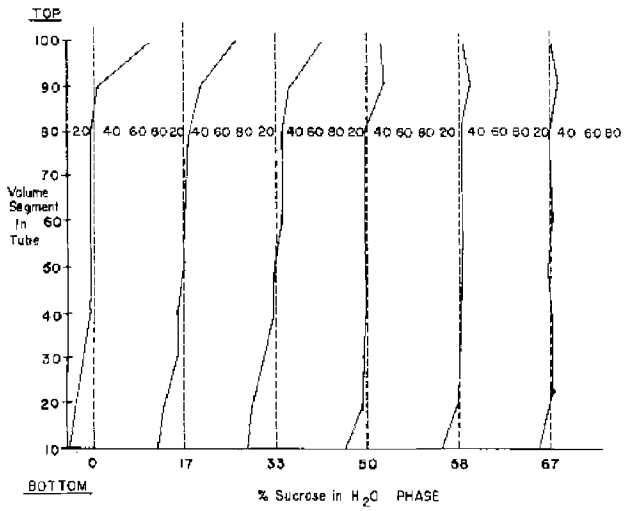


FIG. 2. Oil distribution in liquid emulsions after 30 days storage.

Tekmar Co., Cincinnati, OH). Emulsion temperatures increased from 30 to ca. 60 C during homogenization. All of the emulsions prepared in this report contained 25% liquid safflower oil with the exception of those shown in Fig. 6. In this latter series the oil content was varied over the range 6.25 to 43.75%. In each case the balance of the emulsion consisted of water or a solution of sugar in water at various concentrations as shown in the Figures. Emplex was included at the 1% level in all cases except with Fig. 5 in which a series of Emplex levels (0.5 to 4%) were tested.

Oxygen absorption rates were measured on 20 g samples in duplicate at room temperature in the dark following the method of Bishov (6) with a modification as previously described (7). Emulsion stability measurements were made using pulsed NMR by a method published recently (8,9).

Freeze-dried emulsions were prepared by blending protein, sugar, and/or Emplex. This mixture was dispersed in distilled water at 50 C, safflower oil was added and the emulsons containing ca. 60% $H_2O$ were homogenized using the Tekmar Probe. They were frozen immediately in shallow trays with dry ice and were then freeze-dried for 48 hr.

Average particle size determinations were made on freshly prepared emulsions and on freeze-dried, rehydrated emulsions with a Coulter Counter (Model TAII, Coulter Electronics, Hialeah, FL). All measurements were obtained with a 30 micron aperture cell (10). Porosities of dried powders were measured using an Aminco Porosimeter (American Instrument Co., Silver Springs, MD), following the procedure outlined in the manual furnished with this instrument. Moisture contents were determined on the powders by heating them for 2 hr at 105 C and measuring weight loss in a Brabender Oven (Brabender Corp., Rochelle Park, NJ).

## RESULTS AND DISCUSSION

Results of oxygen absorption rate experiments on liquid oil-in-water emulsions are shown in Figure 1. These are average values for duplicate samples which showed good agreement until oxidation had become extensive. Without any sugar in the aqueous phase, the oxidation rate was rapid with no induction period. But as the level of sucrose was increased, oxidation became progressively slower so that at the highest levels there appears to be strong inhibition.

One possible explanation for this effect is a decreased concentration of oxygen in the aqueous phase as the level

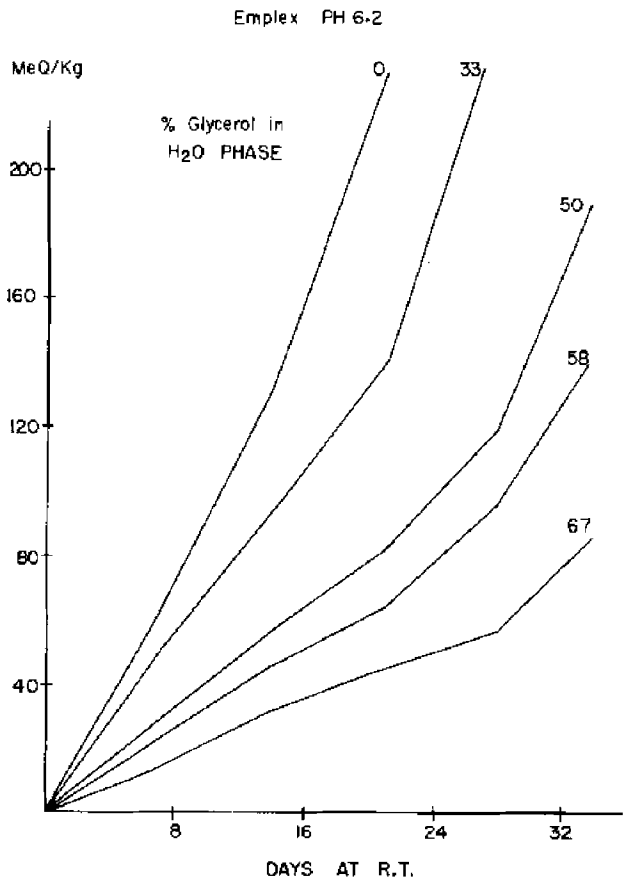


FIG. 3. Oxygen absorption of safflower oil in liquid emulsions containing glycerol.

of sugar is raised. Also at levels of sugar of 50% or more in the aqueous phase the samples became very viscous. We suggest that if diffusion of oxygen through the oil-water interface is rate controlling, then slower rates might be expected as viscosity is increased. It was observed that the very rapid phase of oxidation with many of the samples began only after several weeks of storage. This latter phase coincided approximately with the appearance of creaming. As oil globules rise to produce an oil-rich emulsion near the surface, oxygen should be more accessible.

To determine if there was a correlation between rate of oxidation and stability to creaming, emulsion stability measurements were made on the samples in Figure 1 (8,9). Samples were stored in constant-bore tubes, and at intervals in the distribution of oil throughout each tube was determined using pulsed NMR. One example of the results obtained, after 30 days storage, is shown in Figure 2. The vertical dotted lines represent the oil distribution in the tubes as originally prepared. During storage the distribution changes so that the upper portions become enriched while the lower portions become more lean. As the percentage of sucrose in the emulsion increases, the amount of creaming, as measured by the cumulative deviation from the vertical dotted line, becomes progressively less.

The storage test shown in Figure 1 was repeated with a similar series of samples except that succinoylated monoglycerides (SMG), adjusted to pH 7.0, were substituted for Emplex. The results were almost identical to those shown in Figure 1. When sorbitol was substituted for sucrose, using Emplex at pH 6.2 as surfactant, the results also resembled those shown in Figure 1. In the interests of brevity these data have not been included.

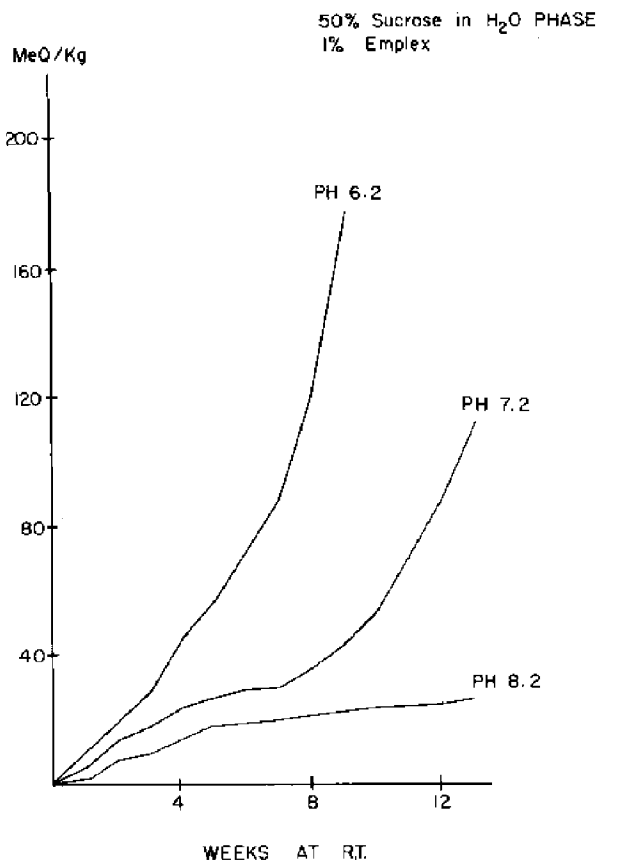


FIG. 4. Effect of pH on oxygen absorption of safflower oil in liquid emulsions.

When either glycerol or dextrose was used with Emplex (Fig. 3), oxidation rates were more rapid with all the samples. But the same pattern of reduced rates at higher carbohydrate levels still held. Only the results for glycerol are shown here since those for the dextrose series were quite similar. Viscosities of emulsions containing either dextrose or glycerol are much lower than those containing comparable levels of sucrose. Also the sucrose-containing emulsions are more resistant to creaming than are those containing dextrose. In all cases, the samples without added carbohydrate creamed within the first few days of storage, and they oxidized rapidly with no induction periods.

Figures 4 and 5 illustrate the effects of pH and emulsifier concentration on oxidation rate. At the same level of sucrose (50% in $H_2O$ phase) stability to oxidation improves over the pH range 6.2 to 8.2. There is a corresponding decrease in extent of creaming at the higher pHs probably due to a greater negative charge on the oil droplets as more anion migrates to the oil-water interface. Raising the level of surfactant from 1 to 2% had a marked effect on resistance to oxidation. Our results also showed improved stability to creaming at this higher surfactant level.

All the experiments described thus far were run at a 25% level of safflower oil in the emulsions. Figure 6 illustrates the effect of variations in oil level over the range 6.25-43.75%. A steadily increasing resistance to oxidation is observed as the oil level is increased incrementally. In this series the sucrose level was held constant while water content was the variable. It appears that the sugar/$H_2O$ ratio is the factor which correlates with oxidative stability. In this storage test, the emulsion weights were adjusted so that each sample contained the same amount of oil.

Having demonstrated that certain sugars and sugar

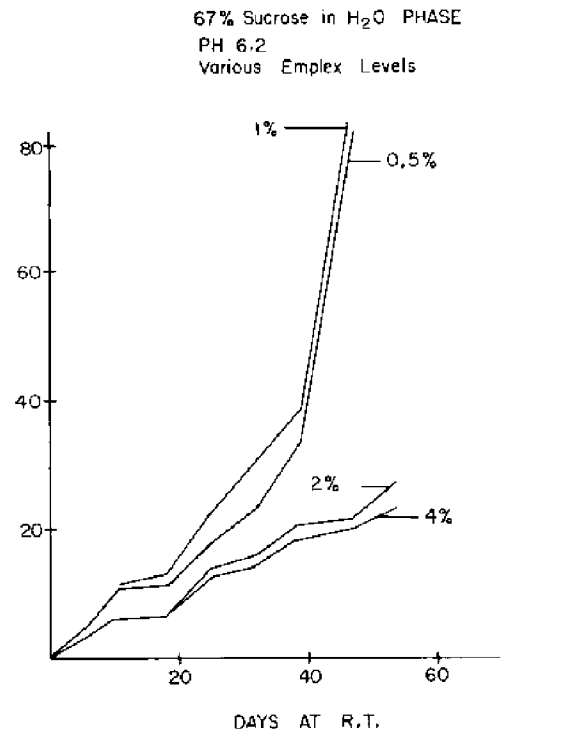


FIG. 5. Effect of Emplex level on oxygen absorption of safflower oil in liquid emulsions.

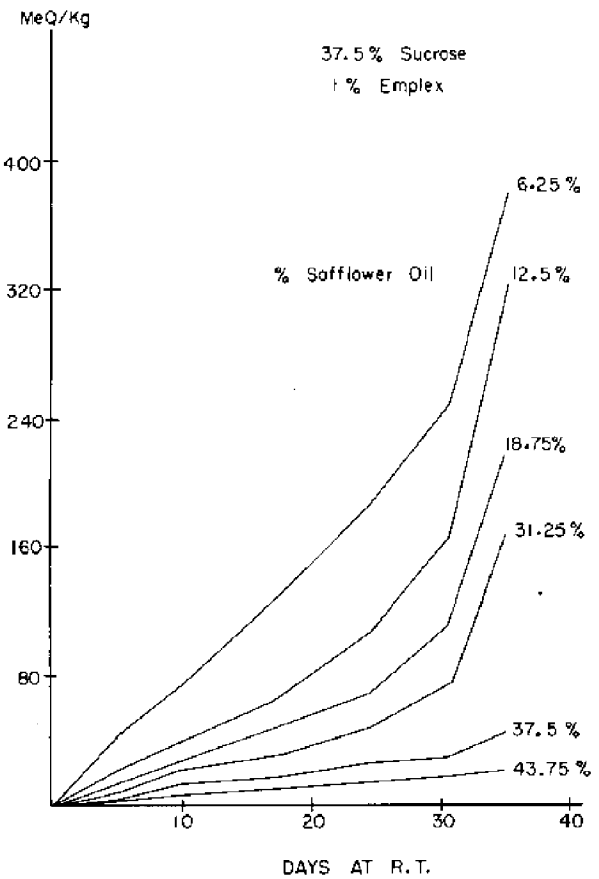


FIG. 6. Effect of safflower oil level on oxygen absorption in liquid emulsions.

TABLE I

Freeze-Dried Emulsions

| Sample % | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Safflower oil | 90.9 | 83.3 | 76.9 | 71.5 |
| Sodium caseinate | 9.1 | 8.4 | 7.7 | 7.1 |
| Sucrose | --- | --- | 15.4 | 14.3 |
| Emplex | --- | 8.3 | --- | 7.1 |
| $H_2O$ | 0.28 | 0.30 | 0.40 | 0.10 |
| With promine D-sucrose | | | | |
| $H_2O$ | 0.33 | 0.10 | 0.70 | 0.22 |
| With promine D-dextrose | | | | |
| $H_2O$ | 0.33 | 0.10 | 1.20 | 1.30 |

alcohols appear to stabilize safflower oil in liquid emulsions, the tests were then extended to freeze-dried systems. It was necessary to introduce a matrix material so that drying could be accomplished to yield free-flowing, homogeneous powders. Sodium caseinate and soy isolate (Promine D) were used to prepare emulsions containing ca. 60% $H_2O$ as shown in Table I. The dried powders contained residual moistures in the range 0.1 to 1.3%. Over this range, the moisture content appeared to have no effect on oxidation rates. Figure 7 shows that samples 1, 2, and 3, which contained protein, protein and Emplex, or protein and sugar, respectively, oxidized more slowly than did the control which was safflower oil alone. Sample 4, however, which contained protein, Emplex, and sugar oxidized significantly faster than did the control. This experiment was repeated three times as shown in Table I, with sodium caseinate and sucrose, with Promine D and sucrose, and with Promine D and dextrose. All three experiments gave results very much like those shown in Figure 7.

In an attempt to explain these unexpected results, the sizes of the oil droplets, before drying, were measured using a Coulter Counter. Those samples containing sodium caseinate or caseinate with sugar had an average oil droplet size of about 8 microns, whereas those samples containing Emplex were in the range 1-1.5 microns. But the much larger interfacial area in both of the latter samples does not explain why only one of them oxidized rapidly. After freeze-drying and rehydration, samples 1-3 from Table I increased in size to an average in the range 11-20 microns, whereas sample 4 now had an average oil droplet size of 5 microns. It appears that a combination of sodium caseinate, Emplex, and sucrose gives a highly dispersed system which is stable to coalescence or agglomeration during drying. This means that sample 4, in the dried conditions, contains a very large interfacial area relative to the other samples tested.

Porosity measurements were also made on the dried powders using an Aminco Porosimeter. Porosities (in cc/g) were 0.47 for sample 1, 1.00 for sample 2, 0.71 for sample 3 and 2.28 for sample 4. This means that sample 4 had a porosity which was 2 to 5 times greater than any of the others. Since it had a more open structure, presumably oxygen transfer to the interior should be more rapid.

We believe that the apparent antioxidant effect of sugars and sugar alcohols on safflower oil in emulsions can be accounted for on the basis of the physical properties of the system. In wet emulsions, viscosity and stability to creaming and phase separation may be the determining factors. In the freeze-dried system, the degree of dispersion of the oil droplets and the porosity of the particles may be rate determining. No evidence was obtained that carbohydrates, in the absence of browning reactions, will have antioxidant properties based on their chemical structures.

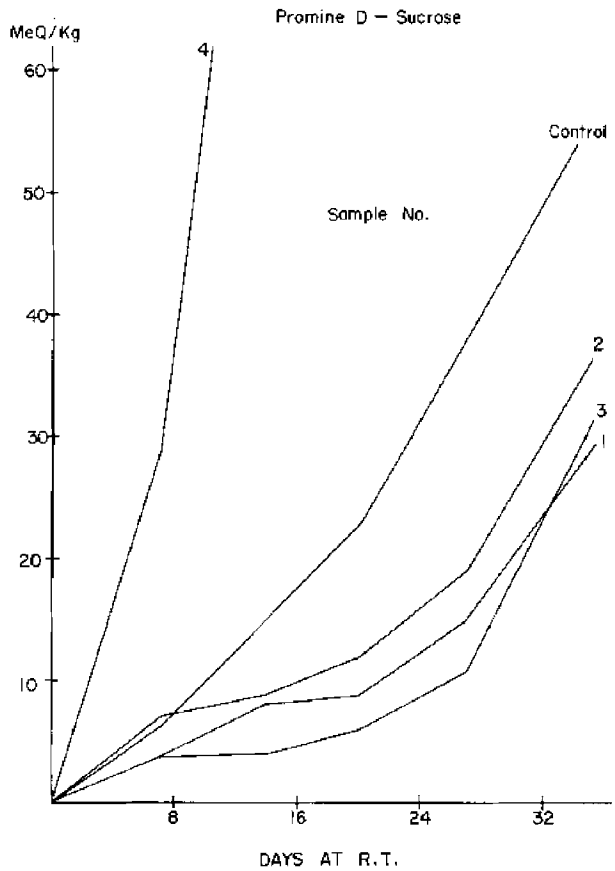


FIG. 7. Oxygen absorption of safflower oil in freeze-dried emulsions.

ACKNOWLEDGMENT

Coulter Counter measurements were made by L. Brennan. R. Engel measured porosities of dried emulsions.

REFERENCES

1. Andrews, F.A., U.S. Pat. 3,429,716, 1969.
2. Mabrouk, A.F., JAOCS 41:331 (1964).
3. Yamaguchi, M., J. Food Sci. Tech, Jpn. 21(4):131 (1974).
4. Rhee, C., and D.H. Kim, J. Food Sci. 40:460 (1975).
5. Sims, R.J., and H.D. Stahl, U.S. Pat. 3,958,033, 1976.
6. Bishov, S.J., and A.S. Henick, JAOCS 43:477 (1966).
7. Fioriti, J.A., M.J. Kanuk, and R.J. Sims, Ibid. 52:219 (1974).
8. Trumbetas, J.F., J.A. Fioriti, and R.J. Sims, Ibid. 54:433 (1977).
9. Trumbetas, J.F., J.A. Fioriti, and R.J. Sims, Ibid. 55:248 (1978).
10. Rowe, E.L., J. Pharm. Sci. 54(2):260 (1965).

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