The curve derived from values in Table II with olive oil acids was used to determine the linolenic acid content of a specimen of soybean oil fatty acids.

TABLE II
Resumé of Linolenic Acid-Hexabromide Data

Linolenic acid, mg.	Hexabromides, mg.	
	Alone	With olive oil acids
1500	1440	1416[1]
1000	940	906[2]
350	293.3	277.8[3]
100	43.8	40.2[3]
50	14.1	10.3[3]
35	....	1.8[3]
25	tr.	0 [3]

[1] With 0.5 cc. olive oil acids.
[2] With 1.0 cc. olive oil acids; with 2.0 cc., this value is 898.
[3] With 2.0 cc. olive oil acids.

TABLE III
The Linolenic Acid Content of a Specimen of Soybean Oil Fatty Acids, as Evaluated From the Standard Curve. Effect of Altering the Bromination Conditions

Soybean acids, mg.	Hexabromides, mg.	Linolenic acid, mg.[1]	Linolenic acid, per cent	Modification of method
2014.6	112.3	178.3	8.85	None
2003.2	111.9	177.9	8.88	None
2002.6	111.8	177.0	8.84	None
1997.7	42.3	102.3	5.12	2.5 cc. of alcohol added before bromination
2006.0	118.5	184.6	9.20	1 cc. glacial acetic acid
1989.8	102.9	167.1	8.04	Brominated at 15°

[1] From curve.

In Table III they are compared with results of the same specimen as observed when the conditions of bromination are altered.

Summary

1. Varying amounts of a specimen of pure linolenic acid have been brominated and the hexabromide yields have been determined by an empirical procedure. The acid was brominated alone and in the presence of olive oil fatty acids.

2. It is suggested that linolenic acid can be specifically and quantitatively determined in fatty acid mixtures by interpolation from a curve showing the linolenic acid-hexabromide yield relationships over the range cited.

3. The empirical nature of the hexabromide yield is confirmed.

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The Study of Aluminum Soap-Hydrocarbon Systems: Effect of Additives and Metathesis[1]

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THE behavior of systems containing only an aluminum soap, such as di-laurate, and a hydrocarbon has been accounted for by the existence of two phases, each stable over a range of temperature and composition: a *gel* of swollen lumps of soap, and a homogeneous isotropic phase called *jelly* or *sol* depending on its rigidity, which varies continuously from a thin liquid when hot and dilute to an elastic semi-solid when cold and concentrated. The transition between these two phases has been described (4) as well as the effect of time and temperature on the viscosity of the jelly (5).

Napalm, a thickener of gasoline for flame warfare purposes, is essentially a mixture of aluminum disoaps and shows the same type of behavior as a pure soap (6). At room temperature it rapidly forms a jelly in gasoline.

Impurities or added materials are known to have a great influence on the viscosity and stability of these jellies and have also been shown to influence the swelling of the soap and the temperature of transition from gel to jelly (4).

In the present paper we describe a few experiments showing the variety of effects produced by different additives on a given soap, and by the same additive on similar soaps, and show that one of the possible mechanisms of action of additives is metathesis between acidic additives and the soap.

Variety of Effects

Experimental. In most of these experiments jellies of 4.00% weight/volume of a Napalm in commercial gasoline containing M/8 or M/40 additive were used. Soap samples of approximately 1 gram were placed in 100-cc. screw-top bottles and brought to the same moisture content by being stored overnight together in an evacuated desiccator. Their exact weights were then determined and the necessary volume of gasoline containing additive added. The systems were gently shaken until no visible settling occurred ("stir-time") and the "set-time," when the gel held a definite shape, was noted. After a day or more, the apparent relative viscosity of the undisturbed jelly in each bottle was estimated by measuring the velocity of fall of steel balls with the help of a traveling microscope and a stopwatch. In Newtonian liquids the rate of fall of spheres is proportional to the square of their radii and the value tr^2/l is a constant. In pseudo-plastic jellies it generally decreases, but variations of tr^2/l with r give an indication of the tendency of the jelly towards pseudo-plasticity if

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[1] Presented before the Division of Colloid Chemistry at the 113th meeting of the American Chemical Society, April 19, 1948, in Chicago, Illinois. Study conducted under Contract OEM-1057 between Stanford University and the Office of Emergency Management, recommended by Division 11.3 of the National Research Council, and supervised by Prof. J. W. McBain.

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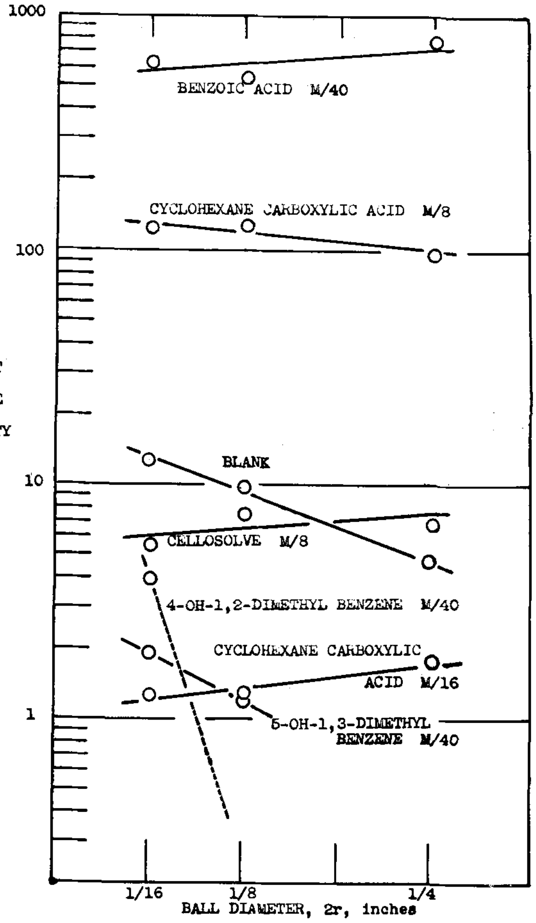

FIG. 1. Effect of additives and the apparent viscosity of 4% Napalm (Ferro-Enamel 493) jellies as measured by falling balls of varying diameters. (The plasticizing effect of 4-OH-1, 2-dimethyl benzene was so marked that the $\frac{1}{8}$" ball fell too rapidly for timing as indicated by the line drawn through one point only.)

decreasing and Newtonian or dilatant behavior if increasing, although the phenomenon may be much more complicated (7).

Results. A few characteristic results obtained are summarized in the figures. From the study of a large number of such data (3), it was apparent that the additives had several different and independent effects on the behavior of these systems,

Stir-time and set-time were both affected in the same direction. Some additives were "retarders," for example cyclohexane carboxylic acid M/8 extended the stir-time from $2\frac{1}{4}$ to 4 minutes and the set-time from $4\frac{1}{2}$ to $18\frac{1}{2}$ minutes, others were "accelerators," for example M/8 fatty acids from C_6 to C_{18} which shortened both times by over 50%.

The effect upon the apparent viscosity was either a lowering by "softeners" such as xylenols, nitrobenzenes, alcohols, or a raising by "stiffeners" such as M/40 benzoic acid or M/8 cyclohexane carboxylic acid. Whether the viscosity was raised or lowered, the jelly could be rendered more pseudo-plastic by "plasticizers" such as 4-OH-1,2-dimethyl benzene or more Newtonian (or dilatant) by "dilatants" such as cellosolve or cyclohexane carboxylic acid (Fig. 1).

There seems to be no simple connection between the three pairs of opposite effects, and examples of additives causing every combination of two effects, such as softener-retarder, softener-accelerator, etc., have been encountered, as shown in Table I.

Closely related compounds can have widely differing effects, as shown by the retarding effect of fatty acids below C_5 and the accelerating effect of those above C_5 (Fig. 2), or the plasticizing effect of xylenols, where the 5-OH-1,3-dimethyl compound has little effect, while the 4-OH-1,2-dimethyl one is one of the most active plasticizers encountered.

TABLE I

Different Combinations of Effects Produced by Various Additives on Jellies of Napalm (Imperial NR232) in Gasoline

Effect	Additive
Softener-accelerator	Lauric acid
Softener-retarder	Butyric acid
Stiffener-accelerator	N-wood rosin
Stiffener-retarder	Benzoic acid
Softener-dilatant	Oleic acid
Softener-plasticizer	4-OH-1,2-dimethyl benzene
Stiffener-dilatant	Benzoic acid
Stiffener-plasticizer	Cyclohexane carboxylic acid

Furthermore, the same additive may have different effects depending on the concentration in which it is applied. Thus cyclohexane carboxylic acid is a softener when M/16 and a stiffener when M/8 for a 4.0% Napalm gel, and N wood rosin approximately halves the viscosity when M/40 and raises it 10,000-fold when M/8.

An effect may also depend on the time at which it is measured, for example at 24 hours benzoic acid M/40 and cyclohexane carboxylic M/8 are both strong thickeners, increasing the apparent viscosity 25 and 40 times, respectively. After 1,000 hours the former is an even better thickener (50 times), but the latter has a much smaller effect (2 times).

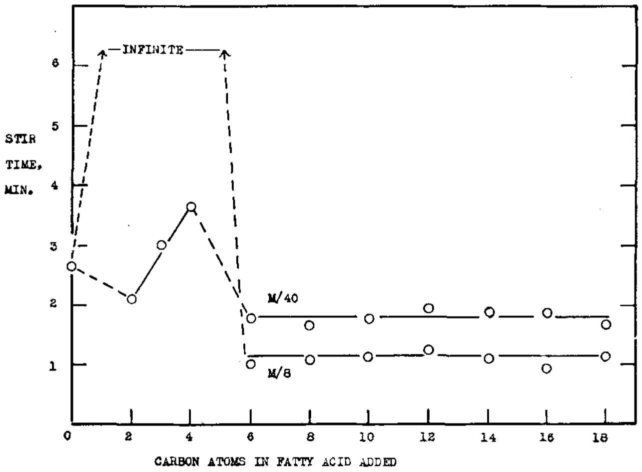

FIG. 2. Effect of aliphatic acids of varying chain lengths on the stir and set time of 4% Napalm (Ferro-Enamel 493) jellies.

Finally, the same additive applied under otherwise the same conditions may have a different effect upon soaps, as similar as Napalms of two different manufacturers, or even different grain sizes of the same Napalm. Thus palmitic acid M/40 has no appreciable effect on an 8% gel of Ferro-Enamel Napalm but reduced the viscosity of Imperial and California Ink Napalm gels by more than one-half. Caproic acid M/40 retarded the setting of 6-20 mesh soap but accelerated that of less than 6-mesh one.

Metathesis

It must be noted that similar effects of additives may be produced in systems of other soaps and even in systems involving no soaps. It is unlikely that such a multitude of effects by such different additives has a simple or single cause. It seems likely that in many cases the additives increase swelling and lower viscosity by themselves satisfying the aggregative forces which normally act between the gelling particles. In case of soaps, however, and furthermore in the case of additives having active hydrogen, an important possible mechanism is that of double decomposition, forming an aluminum compound of the additive and liberating fatty acid.

In order to examine the problem in a simpler system, exploratory observations were conducted on the behavior of aluminum soaps derived from C. P. fatty acids in a large excess of iso-octane, in which swelling but little solution occurs. The degree of swelling and dispersion of the soap depends on the parent fatty acid, the stearate swelling least, the oleate most. The addition of parent fatty acid exerts a marked dispersing influence in all cases. In systems involving two different acids, the final state is quite similar whether the soap was originally formed from one acid or the other. Thus aluminum oleate in the presence of stearic acid tends, within a few days, to behave like aluminum stearate in the presence of oleic acid. The oleate then swells much less than alone, the stearate much more than alone.

This in itself shows that metathesis occurs between fatty acids and the soap. Separation of phases in highly-swollen aluminum soap systems and analytical demonstration of such reaction is, however, rather difficult. Fortunately this can be done in a closely-related system; aluminum di-laurate in benzene to which benzoic acid is added forms a relatively dense and insoluble aluminum benzoate precipitate which may be separated and analyzed.

Other compounds besides fatty acid having active hydrogens may react with aluminum soaps. Thus about 15% of aluminum di-laurate and 10% of water in Nujol produced a white opaque phase upon heating to 320°C. in a sealed tube. This phase was insoluble even at 300°C., and when separated was found to be alumina formed by hydrolysis and free of fatty acids.

Effects of Metathesis. Thus it is likely that in the case of many additives, instead of having simply a jelly of Napalm in a gasoline solution of additive, one soon has, at least in part, a jelly of aluminum "additivate" in a gasoline solution of Napalm acids and that gradually a state of equilibrium is reached. Cawley *et al.* (1) have found that such jellies tend to reach an almost constant state after some time. We have noted that while during the first days the apparent viscosity of jellies containing additives changes much more rapidly than that of controls, after 20 days almost all jellies change very slowly.

Occurrence of this mechanism was first suggested by the behavior of Napalm gels in the presence of benzoic acid, which has a stiffening and retarding effect at lower concentrations, and at higher concentrations leads first to syneretic systems and then prevents gellation completely, leading to an obviously two-phase system (Fig. 3). In the latter cases Napalm seems to disappear partially as such and to be replaced by non-swelling platelets.

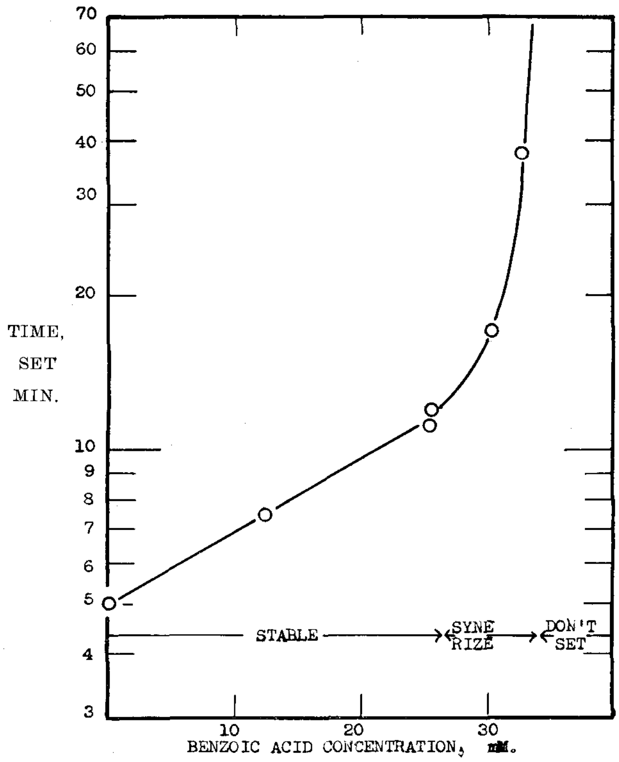

FIG. 3. Effect of varying concentrations of benzoic acid on the set-time and stability of 4% Napalm (Ferro-Enamel 493) jellies.

This made it probable that acids giving an insoluble (or at least non-jellying or gelling) aluminum salt such as benzoic or acetic acid, if present in sufficient concentration, could prevent setting completely by decomposing the Napalm. At low concentration they act as retarders, decomposing some of the Napalm and precipitating the insoluble salt on the surface of grains. This precipitate may cause a stiffening of the jelly perhaps by a cross-linking effect or purely mechanically. Inert fillers may have the same stiffening effect (2). An intermediate concentration (about 30 mM Benzoic acid) the jelly sets at first slowly, but as reaction proceeds the benzoate finally prevails and syneresis occurs.

Experimental

Aluminum Benzoate. Clear benzene solutions containing 2 moles of benzoic acid for each mole of aluminium di-laurate, when poured together, produced a white extremely light precipitate which appeared within a few seconds and slowly settled on standing. The precipitate was separated by filtration, washed with benzene, and dried. The filtrate was evaporated, dried thoroughly and ashed, but no ash was found. This showed that all aluminum had been precipitated. The acid obtained from the decomposition of the precipitate had a neutralization number of 442 mg. KOH per gram, corresponding to a mixture of about 90% benzoic and 10% lauric acid. It melted between 100 and 120°C. (lauric acid melts at 48°C., benzoic at 121.7°). Thus the precipitate was mainly aluminum dibenzoate. In another experiment 3.11 grams of unextracted solid aluminum di-laurate (containing free and loosely bound acid in excess of a di-soap) were added to 100 ml. of benzene containing 4.35 grams of benzoic acid. After standing overnight the precipitate was processed as above. The ash of the dried residue was 17.7%, the filtrate was ash-free. The neutralization number of the acids prepared from this residue was 426. This corresponds to about 20% lauric and 80% benzoic acid. The ash value shows that the residue contained slightly less of the average radical than would be required for an aluminum di-soap.

Action of Fatty Acids. The following series of very dilute systems in iso-octane were prepared in screw-cap vials and observed at room temperature:

1. Unextracted soap
2. Extracted soap
3. Extracted and unextracted soaps of same acid
4. Extracted and unextracted soaps of different acids
5. Extracted soap and parent acid
6. Extracted soap and other than parent acid.

Aluminum dilaurate, distearate, dioleate, and also a naphthenate, were used. Eastman Kodak lauric and stearic acid, Merck oleic acid, and a naphthenic "acid" obtained from the Standard Oil Company of California were used for the preparation of soaps and as additives.

Of the extracted soaps the order of decreasing dispersion was: naphthenate, oleate, laurate, and stearate, the first being swollen almost to the point of solution, the last one showing little visible swelling. The unextracted soaps were all more readily dispersed than the corresponding extracted soaps, particularly in the case of the oleate which rapidly dissolved in iso-octane. When the extracted and unextracted soaps of the same acid were mixed, their behavior was at first independent of one another but after a few days they were hardly distinguishable.

If extracted soaps of different acids were placed together in iso-octane, each behaved as though it were alone with no apparent interaction. When two unextracted soaps of different acids were so treated, the soap which would disperse more readily when alone definitely aided in the swelling and dispersal of the other soap, and vice versa. If, on the other hand, an extracted soap of one acid was mixed with an unextracted soap of another acid, a strong interaction was apparent within a day. In all cases, the dispersion or swelling of the extracted soap increased while that of the unextracted soap was reduced. This was particularly striking where complete solution of unextracted oleate soaps was prevented by the addition of extracted stearate while the latter definitely swelled more than when alone.

The use of added free acid with an extracted soap prepared from the same acid caused an increased dispersal or swelling but, in general, did not seem to be as effective as the excess acid already present in the unextracted soap. However, when soaps were placed in contact with a free acid different from their parent acid, it was found that the characteristic effect of the added free acid in dispersing or dissolving any soap corresponded exactly to the dispersibility of its own soap. The naphthenic and oleic acids were the most effective while the stearic acid was ineffective. Indeed, stearic acid had a definite precipitating action upon the oleate and naphthenate.

Summary

Many additives have pronounced and manifold effects on the behavior of aluminum soaps-hydrocarbon systems. Some additives accelerate the formation of jellies, other retard it. Some thicken the jellies, others liquefy them. The mechanism of the action of additives is probably manifold, too. One of the many possible mechanisms is that of metathesis between the fatty acid radical of the soap and acidic additives. The actual occurrence of such metathesis is demonstrated by both qualitative observations of a variety of systems and by the preparation in benzene of aluminum dibenzoate from the dilaurate.

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