

ACKNOWLEDGMENT

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LITERATURE CITED

- (1) Barrer, R. M., U. S. Patent 2,306,610 (1942).
- (2) Beebe, R. A., Biscoe, J., Smith, W. R., and Wendell, C. B., *J. Am. Chem. Soc.*, **69**, 95 (1947).
- (3) Beebe, R. A., Polley, M. H., Smith, W. R., and Wendell, C. B., *Ibid.*, 2294 (1947).
- (4) Brunauer, S., Emmett, P. H., and Teller, E., *Ibid.*, **60**, 310 (1938).
- (5) Burrell, G. H., and Guild, L. V., U. S. Patent 2,399,095 (1946).
- (6) Dinneen, G. U., Bailey, C. W., Smith, J. R., and Ball, John S., *Anal. Chem.*, **19**, 992 (1947).
- (7) Francis, A. W., and Lukasiewicz, S. J., *Ibid.*, **17**, 703 (1945).
- (8) Hirschler, A. F., and Amon, S., *IND. ENG. CHEM.*, **39**, 1585 (1947).
- (9) Mair, B. J., *J. Research Natl. Bur. Standards*, **34**, 435 (1945).
- (10) Mair, B. J., Gaboriault, A. L., and Rossini, F. D., *IND. ENG. CHEM.*, **39**, 1072 (1947).
- (11) Reyerson, L. H., and Cines, M. R., *J. Phys. Chem.*, **46**, 1060 (1942).
- (12) Wendell, C. B., Jr., *IND. ENG. CHEM., ANAL. ED.*, **18**, 454 (1946).

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NAPALM

Mixture of Aluminum Disoaps

Napalm, the thickener of gasoline for flame warfare purposes, was developed and used in huge quantities during World War II. It is mainly an aluminum disoap of mixed oleic, coconut, and naphthenic acids. In addition to this disoap, Napalm contains also minor proportions of uncombined fatty acids, unsaponifiables, inorganic impurities, and moisture. Its properties are basically determined by the disoap. In this paper the over-all analy-

sis of Napalm, its x-ray diffraction patterns, and behavior in the presence of moisture and of hydrocarbons are presented and compared with those of pure aluminum dilaurate. It is shown that Napalm and aluminum dilaurate are closely akin. Investigation of the pure soap gives, therefore, an excellent basis for the understanding of Napalm and can lead to conclusions unattainable by the study of this mixture alone.

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A PRIVILEGED part of chemical industry deals with products whose structure is largely understood and whose manufacture is subject to logical analysis. Synthetic dyes are an outstanding example of this group. A less privileged part deals with products whose constitution is largely unknown and the manufacture largely empirical. While the former are mostly of recent origin, the latter may be age old, like leather, or new, like streptomycin. The trend is of course always toward a thorough understanding of both product and process with a corresponding increase of efficiency and quality; but often a very high level of performance has been reached by industry long before science cleared its mysteries. Leather, ceramics, ordinary soap, and steel were made expertly long before chemists began to make much progress in their study.

Napalm, the thickener of gasoline for fire bombs and flame throwers, is an aluminum soap developed rapidly (3) and produced in huge amounts since the early years of the war by the precipitation with alum solution of a mixed sodium soap solution, derived from coconut, naphthenic, and oleic acids, and drying the "aluminum soap" thus obtained (1, 4). The product is outstanding among the many commercial aluminum soaps in its ability rapidly to form stable, viscous, elastic jellies (commonly misnamed gels) when placed in gasoline at room temperature. Its efficiency may be judged from the fact that the first mass raid with fire bombs in Japan did more physical damage and inflicted more casualties than the first atomic bomb (15). Yet it was only towards the end of the war that some definite ideas had been gained as to the structure and constitution of Napalm and its jellies with gasoline.

This progress was made possible mainly by careful and an-

alytical work and by the study of pure aluminum dilaurate ($\text{Al}(\text{OHL})_3$), which proved to be an integral part of, and an excellent model for, Napalm. The former was done mostly by Chemical Warfare Service and National Defense Research Committee contractors at Columbia University, Eastman Kodak Company, and Harshaw Chemical Company, while the study of aluminum dilaurate was carried out at Stanford University by a group of which the author was a member.

COMPOSITION OF NAPALM

Napalm can best be considered in terms of soap proper, inorganic impurities, organic extractables, and moisture. Napalms produced at different times and by various manufacturers showed marked variations in composition and properties. There has never been an exhaustive study of one particular batch, and frequently we must use averages obtained from a large series of batches; various data generally refer to different series of batches.

MOISTURE CONTENT. The average moisture content of Napalm, as determined by benzene distillation or by rapid drying in a vacuum oven, is about 0.8%. The agreement between the two methods may be taken as a true value because all the moisture of an aluminum disoap (13) is determined thereby, and almost none of the volatile components is removed from Napalm.

EXTRACTABLES. Extraction of Napalm with dried acetone, in which aluminum soaps are insoluble, shows a rapid removal of soluble material in the first portions of solvent, followed by much slower and slight leaching in successive ones (1). This is similar to the behavior of aluminum disoaps containing uncombined (or molecular) acid, although the break between the rapid and very slow stages seems to be less sharp in the case of Napalm. If the interpretation developed for pure disoap (11) is applied here too, the slow leaching and a small part of the initial rapid extraction are due to hydrolysis of the soap by residual water always present even in the most carefully dried acetone, and the initial extraction removes all the uncombined

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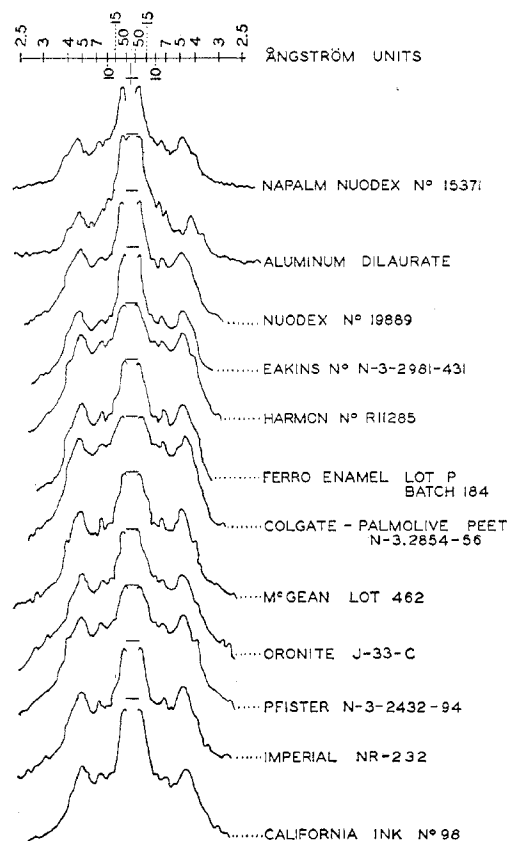


Figure 1. Microphotometer Tracings of X-Ray Diffraction Patterns of 11 Representative Napalms and for Comparison a Tracing of Aluminum Dilaurate

materials. On this basis Napalm contains, on the average, about 7% of uncombined materials (1). Analysis of a typical extract (obtained by extraction with iso-octane) indicates about 30% of unsaponifiables of high iodine value and 70% of free fatty acid.

MINERAL IMPURITIES. Analysis of the mineral constituents of typical Napalms shows the presence not only of aluminum but also of sodium and sulfate. Attributing all the sodium to the presence of sodium sulfate and the excess of sulfate to aluminum sulfate, an average content of mineral impurities of 1.7% has been found (4).

The premises of this estimate may be oversimplified for two reasons. First, some of the sodium dissolved readily in iso-octane and therefore was probably present in the form of sodium

acid soap; secondly, the material insoluble in hydrocarbons when separated by dissolving a Napalm in gasoline (with 5% of nitrobenzene to reduce the viscosity), centrifuged and thoroughly washed seemed to be a very heterogeneous mixture, mostly mixed basic aluminum salts with only a small proportion of normal sulfates of aluminum and sodium (5). The above estimate of mineral impurities, is, therefore, probably somewhat low.

NITROGEN. Kjeldahl nitrogen determinations on two samples of Napalm gave 0.25 and 0.30% (5). The form in which this nitrogen was combined was not investigated, but if it stemmed from protein it might affect markedly (2) the properties of the Napalm.

SOAP. In consideration of the foregoing, about 90% of the Napalm is soap. The fatty acids which go into the manufacture of Napalm have an average molecular weight of about 233 (1) so that the average aluminum content of di-type soaps of these acids would be 5.30%. Actually, on the basis of 1.7% mineral impurities and 90% of soap, the average found for representative Napalms is 5.30%. The agreement may be fortuitous, but nevertheless indicates that the bulk of a typical Napalm has the composition of a disoap ($\text{Al}(\text{OHR})_2$), especially when one contrasts this aluminum content of 5.30% with the values of 9.20 and 3.74% required, respectively, by the mono [$\text{Al}(\text{OH})_2\text{R}$] or tri (AlR_3)-type of soap.

Further confirmation of the view that the bulk of Napalm is a disoap stems from the similarity of behavior of Napalm and of pure aluminum dilaurate with respect to x-ray diffraction, and their behavior with water and with hydrocarbons.

X-RAY DIFFRACTION

The sharpness of x-ray diffraction patterns of Napalms of various manufacturers differs markedly (Figure 1). The same is true of the sharpness of diffraction patterns of pure dilaurate, depending on the method of its preparation (5, 8). However, the over-all pattern of characteristic forms of both is strikingly similar (Figures 1 and 2). There is no indication in the Napalm pattern of either the pattern of aluminum monolaurate (7) or of any of the aluminum oxides (5). Aluminum trisoaps have never been characterized and probably do not exist in the presence of moisture.

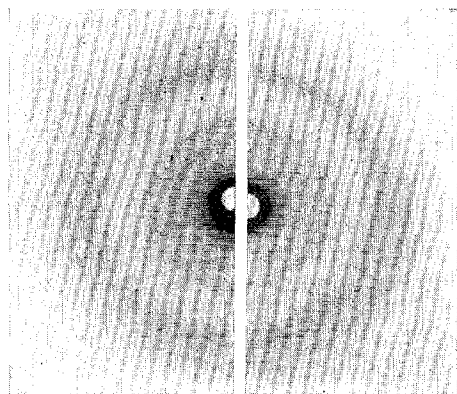


Figure 2. Photographic Reproduction of X-Ray Diffraction Patterns of Napalm Nuodex 15371 and of Aluminum Dilaurate

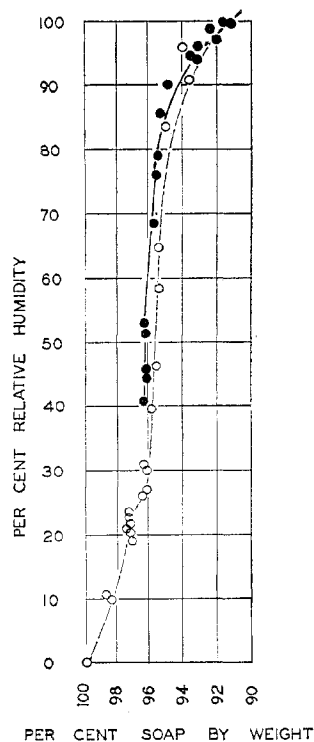


Figure 3. Sorption of Water by Napalm Imperial NR-232 at 50° C.

○ Dehydration
● Hydration

BEHAVIOR WITH WATER

Aluminum dilaurate has little affinity for water, sorbs small amounts of moisture by surface forces only, and is easily and rapidly dehydrated to constant weight. The Fisher reagent indicates for aluminum dilaurate a relatively high moisture content, but this is probably due to reactions involving hydroxyl groups either among themselves or with any fatty acids present (13).

The behavior of Napalm is very similar to that of aluminum dilaurate. Thus it has little affinity for water, as shown by its sorption isotherm (Figure 3), and the moisture sorbed does not affect its x-ray diffraction pattern (Figure 4), showing that here, too, only surface forces are active. The Fisher reagent also indicates much higher moisture contents than other methods, and the

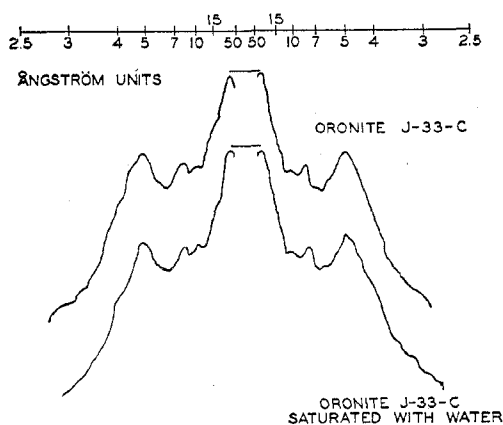


Figure 4. Microphotometer Tracings of X-Ray Diffraction Patterns of a Napalm Dried and Equilibrated with Saturated Water Vapor at Room Temperature

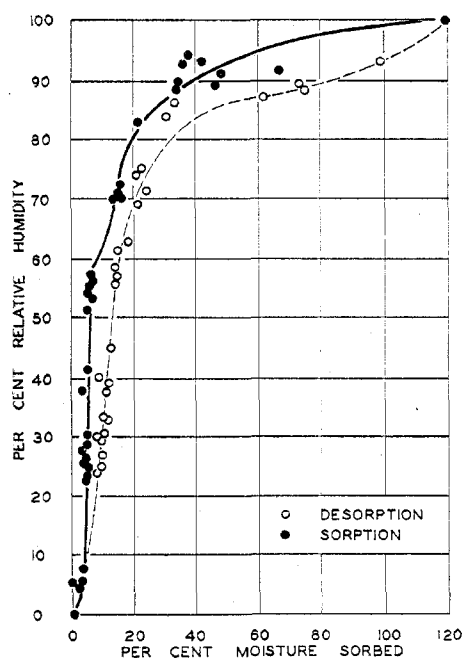


Figure 5. Sorption Isotherm of Water by Inorganic Impurities from McGean 462 Napalm at 50° C.

explanation developed with pure soaps will account for this discrepancy.

On the other hand, Napalm is not readily dehydrated to constant weight. It is susceptible to heat, and reproducible results could be obtained only by observing special precautions (16). Then a rapid loss of moisture occurred followed by further slow loss of about 1% by weight in 10 hours. This was probably due to slow distillation of lower fatty acids (5).

As has been mentioned previously, Napalms always contain inorganic impurities. These sorb moisture readily and exhibit marked hysteresis (Figure 5), and may contribute to the hygroscopicity of Napalm.

BEHAVIOR IN HYDROCARBONS

Both Napalm and aluminum disoaps (6, 9) are capable of forming in hydrocarbons truly stable definite gels of opalescent, discrete, swollen lumps of solid soap; jellies which are transparent, coherent, and elastic; and liquid sols. Temperature, concentra-

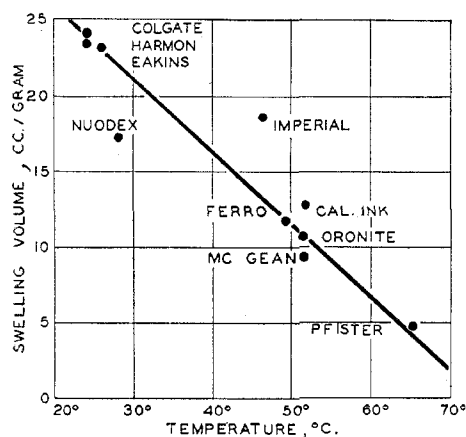


Figure 6. Relationship between the Gel-Jelly Transition Temperature and Swelling Volume after 50 Hours at about 25° C. of 10 Napalms in Iso-octane

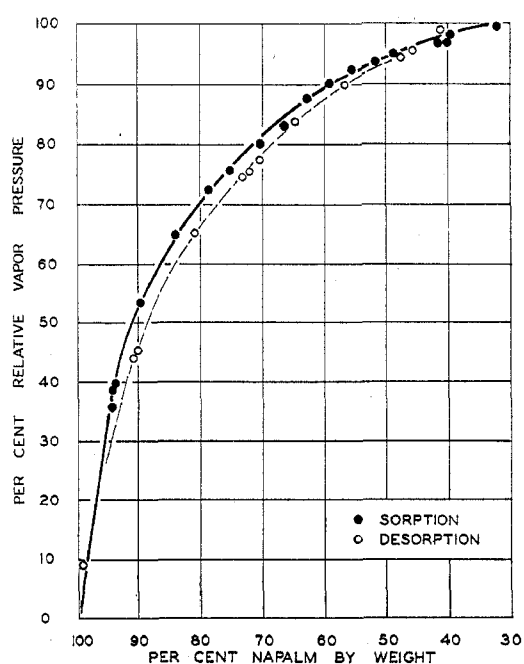


Figure 7. Sorption of Cyclohexane by Napalm Imperial NR-232 at 50° C.

tion, and nature of the solvent all determine which of these systems is formed. For the pure soap, the distinction between gel and jelly is obvious because of the striking clarity of jellies. Napalm systems are somewhat confusing because the mineral impurities remain undissolved and generally form a milky haze throughout the system, whether gel or jelly. Mechanical properties make it possible, nevertheless, to determine the essential presence of jelly. Some solvents, particularly benzene and toluene, have refractive indexes sufficiently close to those of the mineral impurities to render the latter practically invisible, giving clear jellies and sols of Napalm. It is, of course, the jelly which possesses the viscosity and stringiness required for flame warfare purposes.

In dilute systems and with good illumination it is possible to observe the disappearance of the gel on heating and to determine a rather sharp temperature of transition from gel to jelly. This temperature varies markedly among samples of Napalm of various manufacturers and, for a given soap, varies with the solvent. Figure 6 shows the transition temperatures in iso-octane for samples of ten manufacturers. A similar wide variation has been observed for pure aluminum dilaurates prepared under different conditions (6, 10).

For a given sample of aluminum dilaurate there seems to be a regular relation between the swelling of the soap in different solvents and the transition temperature in these solvents (6). The more the soap swells, the lower the temperature at which it changes to jelly.

A similar relation appears in the case of different Napalms in a single solvent, as shown in Figure 6 for iso-octane. The affinity of Napalm for hydrocarbons is perhaps best illustrated by the sorption isotherm of cyclohexane (Figure 7). From an atmosphere of vapor at 95% of saturation pressure the soap sorbs about its own weight of hydrocarbon. The curve is very similar to that of aluminum dilaurate jelly (12) but shows only a small hysteresis.

FACTORS DETERMINING PROPERTIES OF NAPALM

Variations in properties of Napalm could be ascribed to variations in the fatty acid composition, the formation of different mixed soaps, and the presence of foreign components. This is analogous to the way in which the properties of fats and oils may be described. The possible permutations of these factors are so

numerous and analytical methods so imperfect that a quantitative test of such explanations cannot be made at present on Napalm or any commercial soap.

The study of aluminum dilaurate has shown, however, that this pure soap may be changed from a very inert, insoluble, relatively crystalline modification to a very soluble, almost completely amorphous one, and *vice versa*, with many apparent intermediary modifications and their mixtures (10). Here these differences cannot be ascribed to changes of composition or formation of new compounds but probably correspond to variations in the degree and extent of organization and alignment of soap molecules. These forms are mostly thermodynamically unstable but their rate of change is too slow to be noticed in the dry state and at least very slow when in contact with hydrocarbons at room temperature.

This suggests that properties of Napalm and other commercial products are determined not only by the obvious factors first mentioned but also by the modifications in which the soap is present. In fact, once the over-all composition is fixed by the raw materials, this may be the most important determinant.

CONCLUSION

Napalm, being an industrial product, is not a pure disoap whose preparation requires delicate laboratory procedures (14). It differs in two respects. In the first place it contains, as pointed out above, about 10% of impurities—water, inorganic, and extractable materials. In the second place, the remaining disoap does not stem from a pure fatty acid but from a mixture of fatty and naphthenic acids. The average molecular weight of these, 233, is, however, only 15% higher than that of lauric acid, and their content of lauric acid has been estimated at 60%. However, as often happens for mixtures of close homologs, the properties become very similar to those of the individual compound. Thus aluminum dilaurate, whose study as a definite compound is much easier than that of Napalm, serves as an excellent model for this product and has already led to interpretations which could not at present be derived from the study of a mixture.

ACKNOWLEDGMENT

Of the results here reported for Napalm, the x-ray diffraction data were obtained by Sidney Ross and Sullivan S. Marsden, water and cyclohexane isotherms by George W. Shreve, extraction with acetone by Lockhart B. Rogers, Kjeldahl determinations by Earl B. Working, and transition temperatures and swelling in iso-octane by Gerould H. Smith. The study of aluminum soaps was conducted under the direction of J. W. McBain.

LITERATURE CITED

- (1) Broughton, J., and Bayfield, A., Dept. of Commerce, OTS, PB 4193, 31, 71 (1943).
- (2) Edwards, L. J., U. S. Patent 2,420,233 (1947).
- (3) Fieser, L. F., Harris, G. C., Hershberg, E. B., Morgana, M., Novello, F. C., and Putnam, S. T., *IND. ENG. CHEM.*, **38**, 768 (1946).
- (4) Long, K. E., *et al.*, Dept. of Commerce, OTS, PB 4619 (1943).
- (5) McBain, J. W., *et al.*, *Ibid.*, **5885**, 34, 72, 103, 114 (1945).
- (6) McBain, J. W., Mysels, K. J., and Smith, G. H., *Trans. Faraday Soc.*, **42B**, 173 (1946).
- (7) McGee, C., thesis, Stanford University, 1947; Dept. of Commerce, OTS, PB 3885, 98 (1945).
- (8) Marsden, S. S., Mysels, K. J., Smith, G. H., and Ross, S., Dept. of Commerce, OTS, PB 31900 (1946).
- (9) Mysels, K. J., *J. Colloid Sci.*, **2**, 375 (1947).
- (10) Mysels, K. J., and McBain, J. W., *J. Phys. & Colloid Chem.*, **52**, 1471 (1948).
- (11) Mysels, K. J., Pomeroy, H. H., and Smith, G. H., Dept. of Commerce, OTS, PB 31898 (1946).
- (12) Shreve, G. S., *J. Colloid Sci.*, **3**, 259 (1948).
- (13) Shreve, G. S., Pomeroy, H. H., and Mysels, K. J., *J. Phys. & Colloid Chem.*, **51**, 963 (1947).
- (14) Smith, G. H., Pomeroy, H. H., Mysels, K. J., and McGee, C., *J. Am. Chem. Soc.*, **70**, 1053 (1948).
- (15) Stimson, H. L., *Harpers*, **194**, 105 (1947).
- (16) Zentner, R. D., *J. Phys. & Colloid Chem.*, **51**, 972 (1947).

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Solvent Polymerization of Isoprene and Styrene-Isoprene

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Some *tert*-butyl peroxides have been found to be suitable catalysts for the solvent preparation of polyisoprene and the resinous copolymer of styrene-isoprene. In both systems these peroxides gave high yields and were superior to benzoyl peroxide. The polyisoprene shows promise of being useful as a replacement of natural rubber in chemical reactions. The resinous copolymer possesses the properties of a modified polystyrene.

THE purpose of this paper is to describe the preparation of polyisoprene and of a resinous copolymer of styrene-isoprene by polymerization in solvent, using organic peroxides derived from *tert*-butyl alcohol. Solvent or bulk polymerizations are ideally suited for the preparation of clear polymers free from impurities since the system requires no modifying agents other than the solvent medium. A serious problem, however, espe-

cially for diolefins, is the fact that such polymerizations are very slow, and few, if any, catalysts are suitable. Attempts to accelerate the reaction by higher temperatures serve only to decompose the catalyst at a faster rate than it can be efficiently used.

Recent studies (3) showed that *tert*-butyl peroxides have the property of decomposing slowly at temperatures up to 150° C. Since the range 80° to 150° C. is most favorable for promoting rapid solvent polymerization of diolefins, this research was started to determine the value of several representative *tert*-butyl peroxides as catalysts in the preparation of the following two polymers.

POLYISOPRENE

The solvent polymerization of isoprene was studied to determine whether a polyisoprene, free from adulterants, could be prepared. Previous polyisoprenes, which have been tested in