Emulsified Jet Engine Fuel

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SOCIETY OF AUTOMOTIVE ENGINEERS

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PETROLEUM EMULSIONS are commonplace, produced either incidental to recovery, or manufactured for specific applications. The emulsions to be discussed here are made with an essentially single objective -- that of reducing fire hazard. However, in complying with this objective, it is required that the emulsion either be consumable in gas turbine engines or that the fuel, JP-4 in this case, be recoverable for use in aircraft or ground vehicles. These requirements must be met with a minimum weight penalty, thus minimizing the external emulsifying phase, which must not exceed 3%.

The two general types of emulsions are water-in-oil (W/O) and oil-in-water (O/W), and literally thousands of literature citations exist. Possibly the most frequently cited are the O/W types in which comparatively expensive hydrocarbons or hydrocarbon solutions of various agents are the oil phase.

The W/O type of emulsion is often encountered and here the internal water phase is most frequently the minor portion of the composition. Considerably less common are emulsions where the external water phase consists only of a small percentage of the total. O/W emulsions with petroleum internal phases in excess of 70% are relatively scarce. Pickering (1)* early investigated compositions of up to 99% oil,

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*Numbers in parentheses designate References at end of paper.

but such investigations were not frequent, and a more recent one (2) cited 70/30 O/W emulsions of No. 6 fuel oil using sodium oleate formed in situ as the emulsifying agent. Emulsions of liquid fuels containing 15-25% water have been prepared (3).

Emulsion systems high in hydrocarbon internal phase represent a recent emulsion technology, particularly when these systems are designed to reduce hydrocarbon flammability. Highlighting this technology was the "Aircraft Fluids Fire Hazard Symposium" (4) under the auspices of the Daniel & Florence Guggenheim Aviation Safety Center at Cornell University, with staff assistance provided by the U. S. Army Aviation Materiel Laboratories, and the Headquarters U. S. Continental Army Command Aviation Division. Particularly pertinent presentations were those by McCourt (5), Beerhower and Phillippoff (6), Brown (7), Chute (8), and Lissant (9). These papers showed the state of the art, reviewed gelled fuels, cited gelled and emulsion fuel characteristics, feasibility of burning gelled and emulsified fuels in gas turbine engines, and presented test data in the evaluation of emulsified fuels. Another pertinent reference to this emulsion technology is that by Lissant (10) concerned with the relatively recent interest in high internal phase ratio emulsions.

This brief review of the problem provides the background for the balance of this presentation which is concerned with potentially useful emulsifiers (also more generally termed

ABSTRACT

The objective of preparing emulsified jet fuel is to reduce the possibility of in-flight or post-crash fires. Two high internal phase JP-4 fuel emulsions containing 3% external emulsifying phase were developed which have reduced flammability and are engine consumable with low residual ash. One of the emulsions is designed to permit JP-4 recovery for use in other vehicles.

External phase characteristics are described which provide lowered JP-4 volatility and flammability, and which give emulsions stable at -20 to 135 F, are completely resistant to 500 g accelerations, and are corrosion resistant. The effectiveness of various types of emulsifiers and their peculiar requirement for these emulsions are discussed. Preparation, storage, pumpability, and other emulsion characteristics are described.

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surfactants), their selection, emulsion and emulsifier evaluation, preparation, storage, and use requirements.

EMULSIFIER REQUIREMENTS

Requirements for these JP-4 emulsions is that they shall be engine consumable, with a minimum of ash, and that JP-4 be recoverable for use in other vehicles. Dominant requirements other than reduced flammability are that the emulsions shall be thermally stable, withstand an acceleration of 500 g's, be sufficiently viscous that they shall not issue from a 2 in. length hole 1/2 in. in diameter, and be pumpable.

Important in the selection of emulsifier for the completely consumable emulsion is that it be noncorrosive, without adverse effect upon fuel heat value, and that the ash from the emulsion shall be in the range of that from JP-4. Demands for minimum ash will eliminate all inorganic salts of surfactants and dictate the use of amine-type neutralizers. Sulfonates upon combustion will form sulfur oxides which are potentially corrosive, and this may eliminate the large body of sulfate or sulfonate surfactants.

Emulsifiers most nearly meeting the "completely consumable" requirement are compounds comprising carbon, hydrogen, nitrogen, and oxygen. One broad class of surfactants of this type is known as nonionics since in contrast to anionics (the sulfonates) or the cationics (deriving their water solubility from chlorine or bromine), they do not ionize in solution, that is, are essentially neutral. Another class is the amphoterics which possess both a cationic and anionic character in the same molecule, and these can be completely consumable. Cationic agents based on amines neutralized with lower carboxylic acids are another type potentially suitable. Still another class is the complex phosphate esters, where the phosphorus is minimized by the high ratio of consumable organic constituents. This type of compound turns out to be a mild anionic-nonionic surfactant.

Selection of potentially suitable commercially available

candidates of the above types, of published structure and composition, was made from McCutcheon's (12) annual compendium of these agents.

BASIS FOR EMULSIFIER SELECTION

Since there are literally hundreds of commercially available emulsifiers, some method for scientifically selecting them is needed, in addition to the arbitrary classification given above. An approach to this problem is to select a comparatively controlling characteristic which can permit their classification as potentially applicable.

Considering that an emulsion consists of a suspension of in this case, oil-in-water, the agent which promotes this effect must act in some uniform manner to promote the suspension. While there are a number of characteristics of emulsifiers which are measurable and pertinent, the broad aspect in emulsification is to promote suspension of the oil by dissolving in it one end of the emulsifier molecule (the lipophilic end) while the other end remains dissolved in the water (the hydrophilic end). The interface between the oil droplets is then covered with water-dispersible emulsifier and these droplets then resist coalescence by virtue of the self-repelling emulsifier coating. The ratio between the lipophilic and hydrophilic portions of the emulsifier molecule controls its effectiveness. Griffin (11) developed an arbitrary technique for showing ranges of this characteristic called the HLB (the hydrophil-lipophil balance) value. The literature indicates that an HLB value of 12.5 is a near optimum for emulsions of hydrocarbons of the nature of JP-4. In the technique just mentioned, this means that an aqueous solution of the emulsifier should be translucent to clear (range 10-13). The less water soluble surfactants (more oil soluble, 10 or below) show milky to poor dispersions. This simple test provided a means for screening and selecting potentially useful emulsifiers.

Should combinations of emulsifiers have been required to achieve optimum emulsion stability, it is apparent that

Table 1 - HLB Values and Emulsification

Emulsifier	HLB Value	Stability 7 days at 135 F	Emulsion Viscosity (cps $\times 10^{-3}$)
Alamac H26D (Hydrogenated tallow amine acetate)	10-13	No change	90
Emcol CS-136 (Triethanolamine salt of nonyl phenol (6) ethoxy phosphate diester)	13+	No change	100
N-Cocoa-γ-hydroxy butyramide	~8	No emulsion	

the HLB approach would help to systematize and minimize the actual experimental work. Fortunately for this work, single emulsifiers provided suitable emulsions, and determination of HLB by the solubility procedure was the only necessary preliminary to actual emulsion evaluation. Table 1 shows that an HLB value lower than the 10-13 range was a good indicator of lack of effectiveness, and this was verified by other examples.

In this program more than 60 emulsifying agents were preliminarily screened, having been chosen so that members of homologous series were represented to permit HLB optimization. The types of surfactants tested were anionics, nonionics, cationics, amphoterics, and complex phosphate esters (nonionic-anionic in character).

Nonionic compounds may be prepared by reacting ethlene oxide or polyethylene glycol with other compounds possessing a reactive hydrogen group such as carboxy acids, alcohols, amines, amides, or alkyl phenols. Of all the nonionics tested, one series, the Tweens, which are ethoxylates of sorbitan monocarboxy acids, were the only successful ones.

None of the anionics tested (such as true soaps or alkylbenzene sulfonates) proved useful.

Amphoteric agents (containing in the molecule both anionic and cationic groups) and cationics such as quaternaries and amine oxides were generally unsuccessful.

More successful are the fatty amine salts of lower carboxylic acids such as Alamac H26D*, which proved an outstanding candidate, representative of the directly consumable, low ash emulsion.

Another successful class of surfactant is the bi-functional complex phosphate esters reacted with ethylene oxide -- an anionic-nonionic composition. Several of these proved useful, and Emcol CS-136** was the candidate chosen for the recoverable JP-4 emulsion type composition.

EXTERNAL PHASE

Since the external phase cannot represent more than 3% of the total emulsion, its composition must be such that an emulsion is formed in which flammability is reduced, and high and low temperature stability is attained along with other necessary requirements.

While a logical candidate, water cannot be used as the sole external fluid largely because of its low-temperature sensitivity. Its presence in moderate amounts is indicated, however, and it also provides for solubilization of the emulsifier to be used. Nonionic emulsifiers are solubilized by a hydrogen bonding mechanism, water being a material of choice. Other hydrogen bonding fluids are available, and ethylene glycol is a good example, also reducing the freezing point of water. Other glycols and hydrogen bonding agents have been tested or considered, but none has the attractive features or effectiveness of ethylene glycol. Screening tests by emulsion formation have been based upon a 3%

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*General Mills, Inc.

**Witco Chem. Co., Inc.

mixture comprising a 50/50 volume mixture of deionized water/ethylene glycol, and 0.3 wt. % of emulsifier. The latter is measured on a weight rather than volume basis because of emulsifier variation in density and viscosity, since it is used in such small quantities, and is relatively so important.

EMULSION PREPARATION

The mixer used for laboratory investigation is a Hobart Kitchen Aid. The mixer attachment chosen is a wire whip made to travel in a planetary circuit, revolving in a direction opposite to its travel.

Calculated amounts of surfactant are weighed separately and dissolved in the requisite volumes of water and ethylene glycol. This mixture is transferred to the mixer bowl, the mixer started at low speed, and JP-4 added slowly until an emulsion forms (ca. 10%). The balance of the JP-4 is then added moderately rapidly minimizing any large amount of unmixed fuel. With some surfactants, after about two-thirds of the fuel is added, a rubbery, firm gel stage is reached and further mixing and fuel addition may reduce this to a homogeneous, highly viscous emulsion.

High-speed mixers such as a Lightnin' mixer or Premier Dispersator were unsuccessful because the impeller was not capable of thoroughly mixing the composition as it arrived at the highly viscous stage. Large impeller heads designed to give greater contact, such as those used for paint manufacture, were better but still failed to emulsify the JP-4 completely.

For large-scale operations, there are many mixers available for emulsion preparation, but because of the highly viscous character of the emulsion, only a few have been investigated, and these only on a batch basis. A likely candidate device is a Pony mixer which has a single or preferably a double mixer arm, travelling in a planetary circuit, and revolving oppositely to the direction of travel. Such mixers have the power to handle the highly viscous stage and final emulsion, with the necessary mixing action. Peculiarly enough, these emulsions do not necessarily require high speeds or shear, the initial stage from external phase to emulsion occurring with light mixing, followed by more intensive mixing as the oil-in-water phenomenon occurs.

EMULSION SCREENING TESTS

Emulsifier screening consists of HLB determination, and if in the 10 to 13+ category, the preparation of emulsions as indicated above. These emulsions are then submitted to primary performance tests.

PRIMARY PERFORMANCE SCREENING - Following preparation of the emulsions, portions are removed in capped 2 oz jars and stored at -20 F and 135 F. Changes are noted daily for seven days. Another jar is set aside at 77 ± 2 F for 30 days for stability measurement.
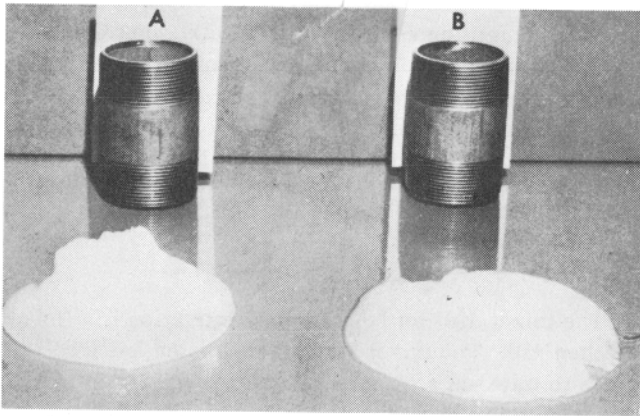
Another portion is subjected to 500 g acceleration ac-

Fig. 1 - Apparent relative viscosity as degree of "slump"
A - Emcol CS-136 emulsion. B - Alamac H26D emulsion

Table 2 - Cleveland Open Cup Flammability Points

Emulsion	Time Lapse, Min.	Ignition Temperature, F
JP-4 Fuel	0	77
JP-4 Fuel	0	77
Emcol CS-136	17	155
Emcol CS-136	18	155
Alamac H26D	15	135
Alamac H26D	16	140

cording to method ASTM D 96 in a centrifuge for 30 minutes and separation noted.

Apparent viscosity is measured with a Brookfield Rvp viscometer using a No. 7 spindle at speeds of 2, 4, 10, and 20 rpm. This is a rapid "control" type procedure, and indicates relative viscosities satisfactorily.

One of the viscosity requirements is that the emulsion shall be sufficiently viscous that it shall not flow through a 1/2 in. diameter pipe 2 in. in length. Using a 6 in. head of emulsion it was found that at 60,000 centipoises (cps) the emulsion would just flow, and that at 230,000 cps the emulsion required 1/4 to 1/2 lb pressure for flow initiation. This suggests about 100,000 cps as a target viscosity to meet this requirement. Table 1 shows that both of the emulsions described elsewhere lie in this range.

Fig. 1 shows the apparent relative viscosity as degree of "slump" after given periods of time.

Unless the thermal, storage stability, and gravity stability tests can be passed, there is no need for further property investigation. Hence these simple procedures effectively and quickly segregate potentially suitable systems.

SECONDARY SCREENING -

Flammability - Flammability of the emulsions is tested using the Cleveland Open Cup procedure according to ASTM 92-57 and the data for two emulsions and JP-4 are shown in Table 2. Another test was made with the Cleveland Open Cup apparatus where the flame was kept continuously over the emulsifier cup until the emulsion ignited. Whereas the JP-4 fuel ignited almost immediately, neither of the two emulsions ignited after an hour exposure at 77 F.

Other flammability control tests are necessary, and the rate of flame travel in an open trough or an open trough with a perpendicular shield to interrupt flame transfer will be made. Another test will be that in which a container of fuel is flung against a grid behind which is a flame source, to demonstrate flammability and type of ignition and pattern upon impact.

Explosivity - Explosivity tests were made using an M.S.A. Model 40 Explosimeter. A Petri dish full of emulsion (as
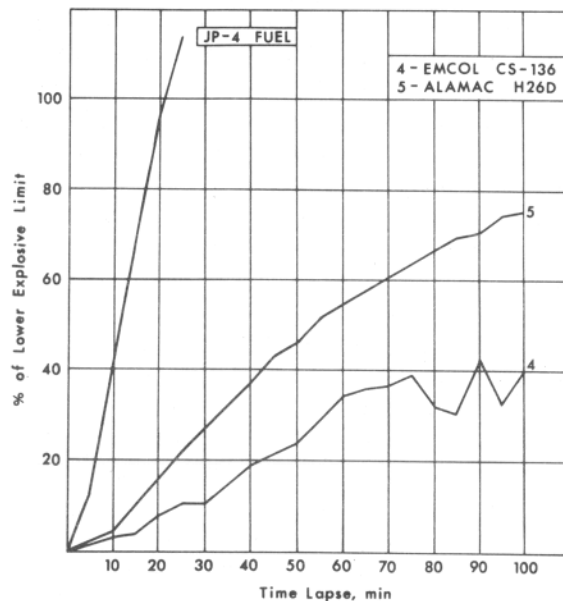

Fig. 2 - Explosimeter tests

in evaporation rate) was transferred to a 5 gal wide mouth jar and the Explosimeter probe inserted through the jar lid to the jar center. Measurements were made at 5-minute intervals and the lower explosive limit (L. E. L.) of the JP-4 fuel in the air recorded (for JP-4 the L. E. L. is 0.6%). These data are shown in Fig. 2. These data show the emulsified fuels reach the L. E. L. of JP-4 only after four to five times the exposure period for the plain fuel.

Corrosion Testing - Since emulsions must be stored or transported, probably in steel drums, the first metal to be corrosion tested was cold rolled mild steel. These tests were conducted at 77 F by coupon partial immersion for 30 days. It was this test that eliminated the Tweens from competition since they were unstable and caused much corrosion. Other aircraft material components likely to contact the emulsion are under test.

Evaporation Rate - Evaporation rate data were obtained at -20 F, 77 F, and at 135 F. Emulsion was transferred to a 3.8 in. wide × 1/2 in. high Petri dish and the surface levelled
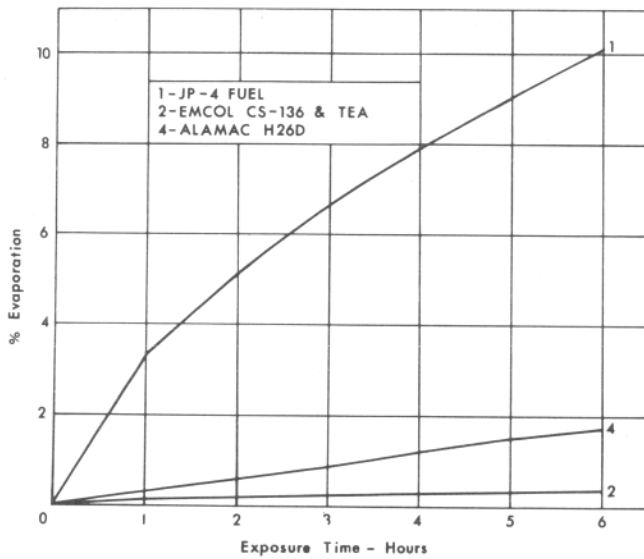
Fig. 3 - Evaporation rate at -20 F
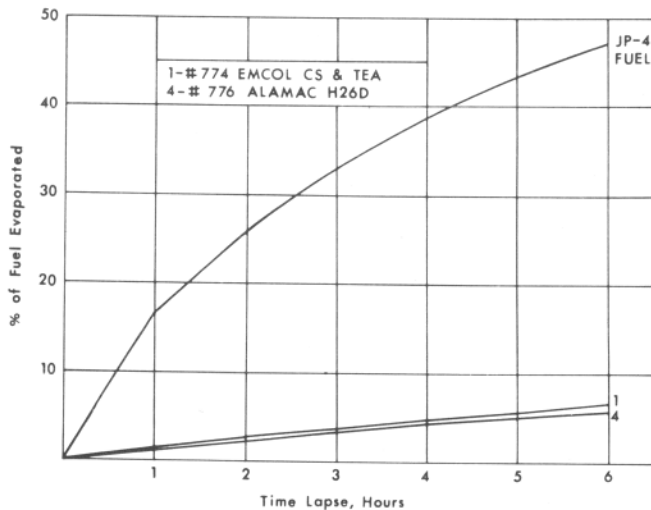

Fig. 5 - Evaporation rate at 135 F

Fig. 4 - Evaporation rate at 77 F

Fig. 6 - Pumped CS-136 emulsion

with a straight edge. Weight losses were measured at hourly intervals. Results of these tests are shown in Figs. 3-5. These data demonstrate the lowered volatility of JP-4 in these emulsions, the ratios of JP-4 to emulsions being 5/1 at -20 F, 8/1 at 77 F, and 2/1 at 135 F.

Pumpability - An important requirement for emulsified fuels is that they be pumpable both for transfer and for feed to the engine. Emulsions can be formed by the shear resulting from pumping action and they likewise may be shear-sensitive. Laboratory tests with a 1700 rpm gear pump and a 3400 rpm centrifugal pump indicated that these emulsions were pumpable without breakdown. An interesting and important finding was that neither emulsion readily wetted either glass or aluminum, indicating that fuel hold-up as a result of wetting would not be a likely difficulty. Fig. 6 shows the emulsion being pumped over an aluminum sheet.

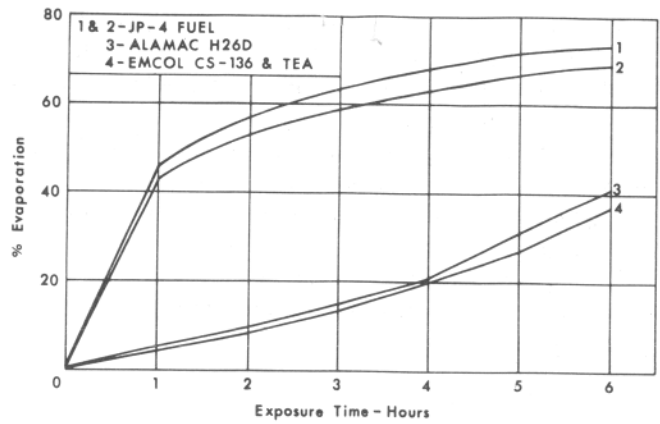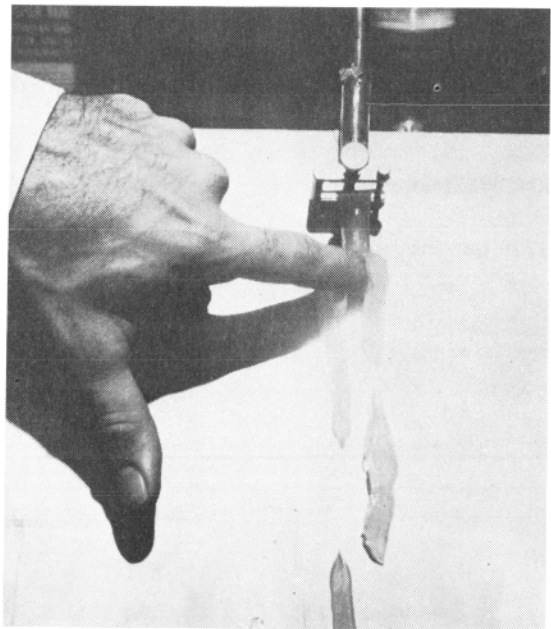Other stability tests are to be performed which will in-

dicate emulsion mechanical shear stability, static charge effect and buildup, lubricity, vapor pressure, heat value, microorganism resistance, and fuel quality characteristics of recovered JP-4 fuel.

JP-4 RECOVERY

A contract requirement is development of a JP-4 emulsion which can be directly engine consumable, with the added stipulation that this composition or another be developed from which JP-4 can be recovered for use in other vehicles at forward areas. The recovered JP-4 is to meet the requirements of MIL-T-5624G except for the water separometer index specification.

Recovery may be achieved by any suitable process such as chemical demulsification, shear, heat, or combination of such approaches. Chemical demulsification is most likely

to be successful with anionic surfactants which can be de-activated by decomposition with acid or with chemicals causing coagulation, as for example with a solution of aluminum salts. Since emulsions are made or broken by the right degree of shear in either case, and since the emulsions must be pumped about, a combination of chemical and shear through high speed turbine pumps appears to be a reasonable, large scale approach. Thus, for this approach, as a loop from which free JP-4 can be recovered as overflow, followed by centrifugal separation and passage through a further de-watering or clarification system, appears to have potential merit.

SUMMARY

As is apparent, this is a progress report rather than a finalized summary of a completed task. It shows that these emulsions can fairly readily be made using satisfactory emulsifiers, that they reduce fire hazard, and that they meet many of the imposed stability and compatibility requirements for such products.

ACKNOWLEDGMENT

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REFERENCES

1. S. V. Pickering, J. Chem. Soc., London, Vol. 91, 1907, p. 2002.
2. Brit. 974,042 Esso Research & Engineering Co., CA Vol. 62, 1965, p. 1503.
3. Fr. 1,357,094, American Viscose Corp. (M. M. Cruz, Jr.), CA Vol. 63, 1965, p. 11,225.
4. Daniel and Florence Guggenheim Aviation Safety Center, Cornell University, Proceedings, June 7-8, 1966.
5. F. P. McCourt, ibid, p. 56.
6. A. Beerbower and W. Philippoff, ibid, p. 86.
7. W. E. Brown, ibid, p. 110.
8. R. Chute, ibid, p. 139.
9. K. J. Lissant, ibid, p. 165.
10. K. J. Lissant, 40th Nat'l Colloid Symposium, Preprints, J. Colloid and Interface Science, 1966, p. 44.
11. W. C. Griffin, Offic. Dig. Federation Paint & Varnish Production Clubs Vol. 28, 1956, p. 466.
12. J. W. McCutcheon, "Detergents and Emulsifiers," 1966 Annual, J. W. McCutcheon, Inc., Morristown, N. J.