GRAPH 1

The bead test value was 40 days compared with 20 hrs. by the A.O.M. If the oil had not been diluted the A.O.M. value would have been still lower. Also, comparing Sample 44 with Sample 45, the influence of dilution is quite evident in the bead test (a rise from 10-11 to 16 days) while the A.O.M. showed virtually no difference (27 hrs. to 28 hrs.). Actually this comparison of the two methods was not sufficiently comprehensive to justify firm conclusions.

Conclusion

It is believed that the above described experiments disclose a method which merits further investigation and application as a means of determining the stability of vitamin A in oils and fats. The values found are reproducible within a deviation of about one day (at large half-way values the absolute variation would probably increase). The times between testing and retesting varied from a few days to about 8 months (sample stored under CO_2 or nitrogen at 5°C.).

An outstanding aspect of the data presented shows the improved stability due to the various antioxidants, for example, Sample 7 compared with Sample 8; Sample 15 compared with Sample 16, etc. Another interesting disclosure is the influence of dilution on stability.

It is important to point out that the value of this (or of any other) accelerated method may not be judged with confidence until the method has been compared with the results of tests under ordinary storage conditions. These storage experiments are in fact under way at the present time but are not yet completed.

It should be pointed out also that the tests described may be still further accelerated by using smaller quantities of oil than those described.

The use of an accelerated test for vitamin A stability, based on surface-expansion, is in better accordance with practical conditions than are other tests because of the practical application of vitamin A oils in dry-feed mixtures, tablets, etc.

Summary

A new, simple, and rapid method is described for evaluating the stability of vitamin A in oils.

The acceleration is obtained at room temperature (20°C.) by spreading the oil over a neutral carrier (glass beads), thus obtaining greatly expanded surface areas, and consequent increased exposure to air.

Comparative tests were conducted involving the Active Oxygen Method ("Swift" test) and, while the results were inconclusive, striking deviations in results were noted.

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The Suppression of Soil Redeposition[1]

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IT IS DESIRABLE to consider the redeposition of soil as a separate entity in the total washing process. Soil redeposition is caused primarily by presence of calcium and magnesium cations found in natural waters and to a lesser degree by the relatively high concentration of sodium ions introduced with the washing composition.

Examining the deposition of carbon from aquadag suspensions and the redeposition of soil in the washing process, P. T. Vitale (1) has recently drawn attention to the large effect produced by electrolytes and particularly to the presence of divalent cations.

In the present study the deposition effects from Aquadag[2] suspensions are examined as quantitatively as possible in order to evaluate the suppression of the

[2] Acheson Colloids Corporation, Port Huron, Mich.

influence of mono- and divalent cations. An arbitrary aquadag suspension is used, and the deposition of this on swatches of clean cotton cloth is measured. This aquadag suspension has been shown to be fairly typical of actual carbon soil, and parallel effects have been obtained between washing naturally soiled laundry and comparable tests with artificial aquadag suspension (1). Suppression of soil deposition could conceivably be achieved a) by elimination of the cations responsible, or b) by protection of the soil and/or cloth substrate from the action of cations (2, 3). Both methods will be considered in this paper, and both methods are commonly used in practice. We wish to ascertain the characteristics and limitations of these procedures.

Experimental

Many previous workers have examined deposition on cloth from a suspension of soil. The general experimental conditions used in the present work were as follows.

A 0.03% aquadag paste suspension was made in 1 liter of distilled water containing 0.035% sodium alcohol sulfate (Duponol ME salt-free, ether-extracted). This solution also contained the salts in the desired concentration to be examined. In this mixture, at 120°F., 10 white cotton cloth swatches 2½ in. x 3½ in. were agitated in a laboratory washing machine consisting of a 2-liter silvered Dewar beaker equipped with a slotted micarta cover and an agitator with micarta blades. After 10 min. of agitation the swatches were removed, rinsed, and dried at room temperature. The change in reflectance was measured with the Hunter Reflectometer, using a turntable so that all 10 swatches could be read at one time (4). This cycle was repeated in some sets of runs from one to 10 times. Since parallel curves were obtained, only the first runs are recorded.

Calcium hard water was prepared by dilution of a known stock solution of calcium chloride. One mol per 1,000 liters is equivalent to 100 p.p.m. measured as $CaCO_3$. The stock solution was equivalent to 5,000 p.p.m. and had pH 7-8.

Results and Discussion

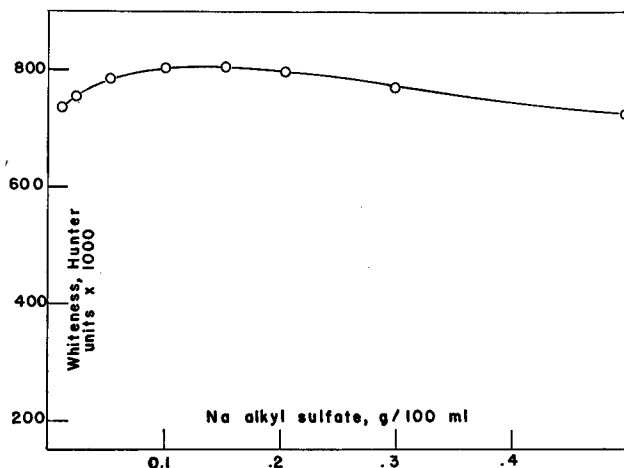The effect of varying concentrations of sodium alkyl sulfate (salt-free duponol ME) in the absence of other salts is shown in Figure 1. It is seen that the effect is small over the range of detergent concentrations studied. The whiteness improves slightly up to about 0.15% and then falls slightly, possibly due to increasing concentration of sodium ion from the sodium alcohol sulfate. A similar form of curve is obtained with sodium myristate in distilled water as seen in Figure 6.
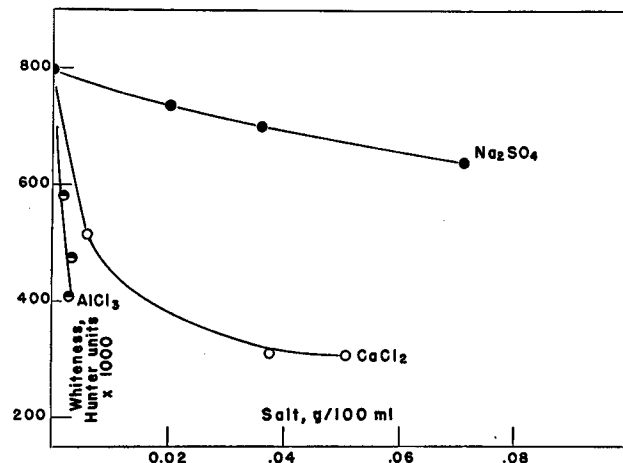

FIG. 2. Deposition at 120°F. with mono-, di-, and trivalent cations. 0.035% sodium alkyl sulfate, 0.03% Aquadag.

Figure 2 shows the effect of mono-, di-, and trivalent cations upon deposition in distilled water. In the case of the polyvalent ions, only the first part of the curves (approximately up to 0.02% salt) should be taken as significant since precipitation and coagulation of the suspension tends to occur when higher salt concentrations are present. Measurements of soil deposition are not valid in nearly exhausted or flocculated solutions. The relative order of the effect is in agreement with the Schultz-Hardy Rule.

Suppression of Soil Redeposition by Suppression of Calcium Ion. The behavior of ortho-, pyro-, tri-, and metaphosphates and sodium sulfate upon deposition in distilled water is shown in Figure 3. The effect of the various phosphates under these conditions is very similar. The salts show marked increased deposition with increase in concentration.

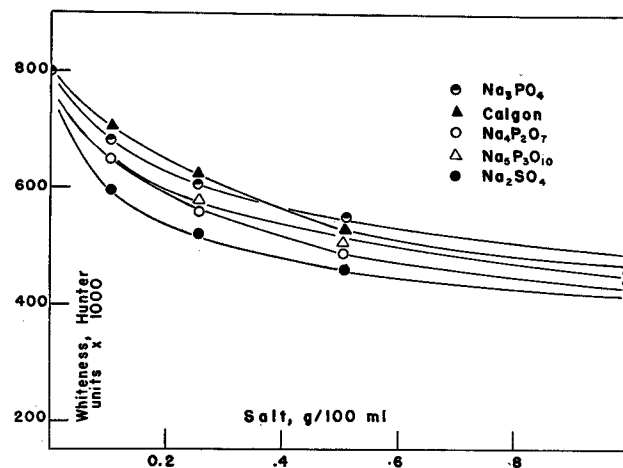The effect of sodium triphosphate upon the deposition of aquadag in the presence of calcium hard

FIG. 1. Deposition of 0.3% Aquadag with varying concentration of sodium alkyl sulfate at 120°F.

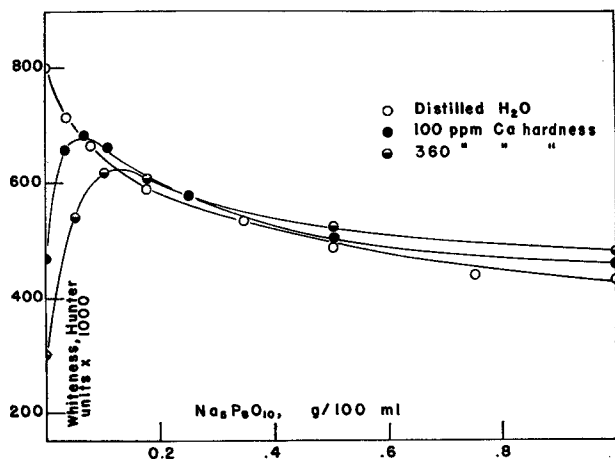FIG. 3. Deposition at 120° F. with varying concentration of salts. 0.035% sodium alkyl sulfate, 0.03% Aquadag.

FIG. 4. Deposition at 120°F. Effect of sodium triphosphate in distilled water, also in 100 p.p.m. and 360 p.p.m. calcium hard water. 0.035% sodium alkyl sulfate, 0.03% Aquadag.

FIG. 6. Deposition at 120°F. Effect of sodium myristate in distilled and hard water. 0.035% sodium alkyl sulfate, 0.03% Aquadag.

water is shown in Figure 4. The initial values on these curves are due to calcium hardness (where present), and it is seen that deposition decreases to a minimum value when the triphosphate completely suppresses the effect due to the calcium hardness. On further addition of triphosphate deposition closely follows the curve for triphosphate as a sodium salt in distilled water.

A similar series of curves is obtained when the tetrasodium salt of ethylene diamine tetra-acetic acid (EDTA) is used instead of triphosphate (Figure 5).

The curves of Figure 4 show that maximum whiteness is obtained with 0.04 g. of triphosphate for 100 p.p.m. solutions and at 0.14 g. of triphosphate for 360 p.p.m. solutions. This corresponds to about 1.2 moles of triphosphate per mole of calcium hardness for complete suppression.

With the tetrasodium salt of ethylene diamine tetra-acetic acid for both 100 p.p.m. and 360 p.p.m. the value is very close to one mole for one mole of calcium (pH 10). These results for triphosphate and EDTA are in close agreement with the values obtained by examination of the amounts of these ma-

terials required to protect the foam of sodium cetyl sulfate in the presence of hardness (5).

Soap is a material which removes calcium ions by precipitation. In Figure 6 is shown the effect of sodium myristate on soil deposition in distilled, 100 p.p.m. and 360 p.p.m. solutions. For 360 p.p.m. solutions 0.3 g. of sodium myristate is required to bring deposition values to the original distilled water line. 0.3 g. of sodium myristate corresponds to about 3.3 moles of soap per mole of calcium hardness. Only 2 moles of sodium myristate should be required for precipitation of calcium soap. The suppression of calcium ion by soap is analogous to that shown by
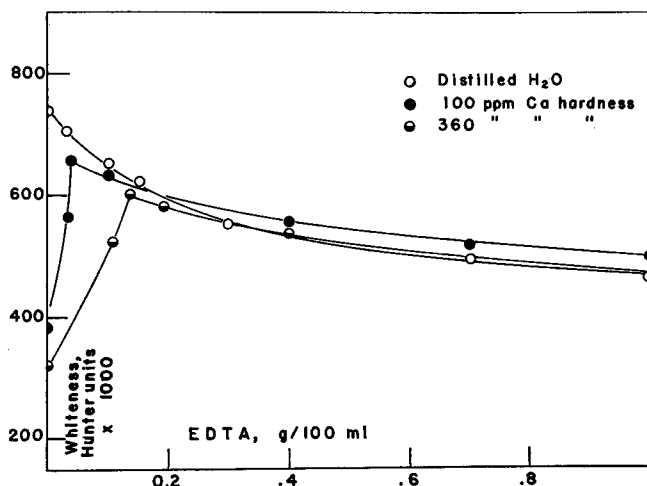

FIG. 5. Deposition at 120°F. Effect of tetrasodium ethylene diamine tetra acetate. In distilled water, also in 100 p.p.m. and 360 p.p.m. calcium hard water. 0.035% sodium alkyl sulfate, 0.03% Aquadag.
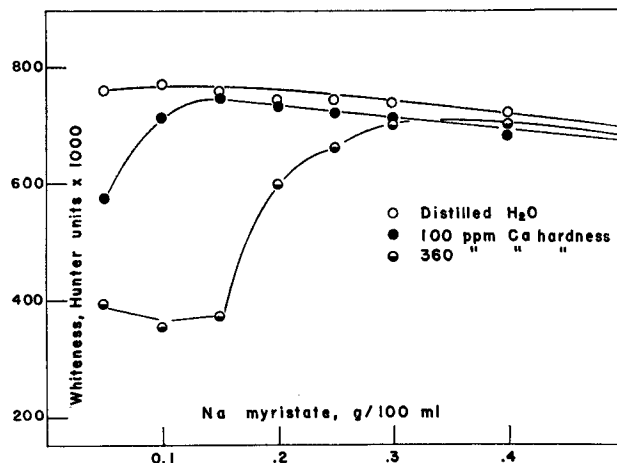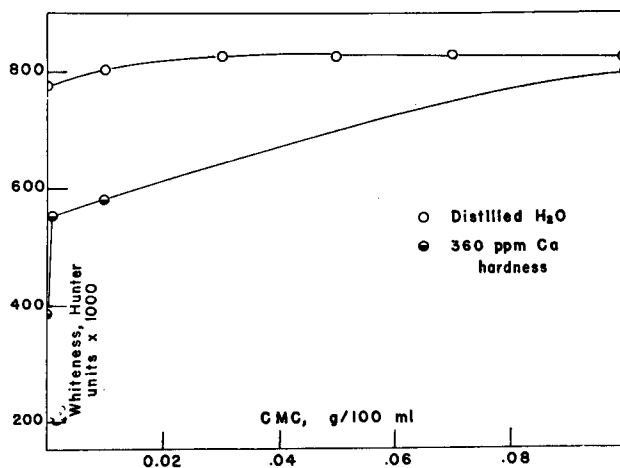

FIG. 7. Deposition at 120°F. Effect of sodium carboxymethyl cellulose in distilled and 360 p.p.m. hard water. 0.035% sodium alkyl sulfate, 0.03% Aquadag.

phosphates and chelates with the difference that after removal of the calcium by precipitation further increments of soap do not cause significant deposition. In the case of the phosphates and chelates further addition beyond the equivalence point produces the characteristic increasing effect of sodium salts on deposition.

Suppression of Soil Deposition by Protection of Soil and Cloth. The inhibition of ionic effects which result in soil deposition can be achieved by protection

of the soil or substrate by polyelectrolytes, such as sodium carboxymethyl cellulose (CMC). Figure 7 shows the effect of increasing amount of CMC in distilled and calcium hard water. 0.1% CMC overcomes the effect of 360 p.p.m. hardness and gives reflectance values almost equal to the original whiteness of the cloth. Figure 8 shows that the electrolyte effect of sodium sulfate can be compensated for by presence of very small amounts of CMC.
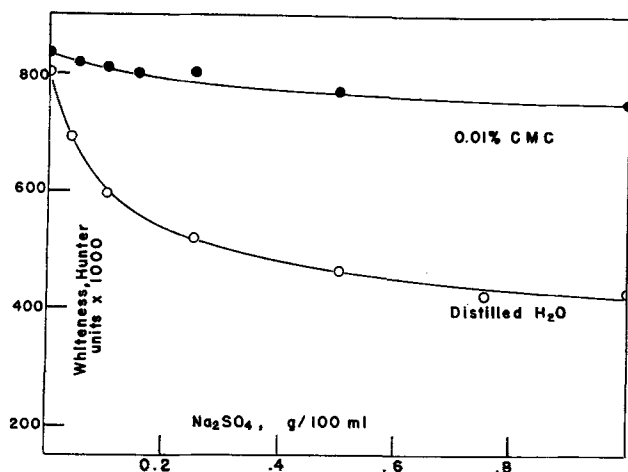

FIG. 8. Deposition at 120°F. Effect of sodium sulfate in distilled water and in presence of 0.01% CMC. 0.035% sodium alkyl sulfate and 0.03% Aquadag.

It is characteristic of many precipitants, chelates, and sequestrants that stoichiometric maxima occur in deposition curves in hard water. Thus the measurement of soil deposition may in certain cases be regarded as a form of approximate titration for divalent hardness. CMC shows no such stoichiometric relationships. A further distinction between CMC and the calcium ion suppresants is that CMC inhibits soil deposition in the presence of mono- as well as polyvalent ions.

Examination of the amount of CMC required for protection of the foam of sodium cetyl sulfate calcium hardness (5) has shown that this material has almost no calcium ion suppression value. At 10 p.p.m. hardness there is a protection effect at a ratio of 100-200 parts of CMC to 1 part of $CaCO_3$, but at greater hardness there is no protection of the foam.

Vaughn and co-workers have examined systems of detergent and CMC in mixes with various carbonate builders (6) and clearly demonstrated the value of CMC in these systems.

Suppression of Soil Redeposition Using Practical Detergent Mixes. In Figure 9 three concentrations of detergent (sodium salt of alkyl aryl sulfonate) were mixed with varying amounts of sodium triphosphate and examined for soil deposition in 21 g. water (360 p.p.m.) of mixed magnesium and calcium hardness.[3] The maxima are independent of the concentration of detergent and are a function of the stoichiometric relationship of the water hardness to the triphosphate required. Hence, for a given amount of hardness, the same amount of triphosphate is required for suppression of the deposition effect due to hardness, and it is

[3] The mixed hardness contained 3 parts calcium hardness to 1 part magnesium hardness measured as $CaCO_3$ equivalent.
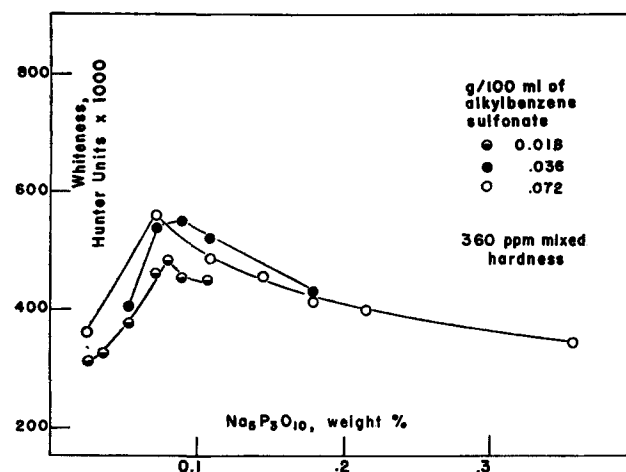

FIG. 9. Deposition at 120°F. in 360 p.p.m. mixed hard water for three concentrations of detergent and varying concentration of sodium triphosphate.

seen that the maxima of all three curves occur at approximately the same triphosphate concentration.

Figure 10 shows the salt effect at 120°F. in distilled water for sodium carboxy methyl cellulose, sodium myristate, tetrasodium ethylene diamine tetra-acetate, and pentasodium triphosphate.

This discussion is restricted to a consideration of soil deposition in systems containing carbon soil, hardness, detergent, protective agent, and cloth substrate. The major or gross effects must be expected to remain as a definite pattern upon which minor effects may be superimposed.
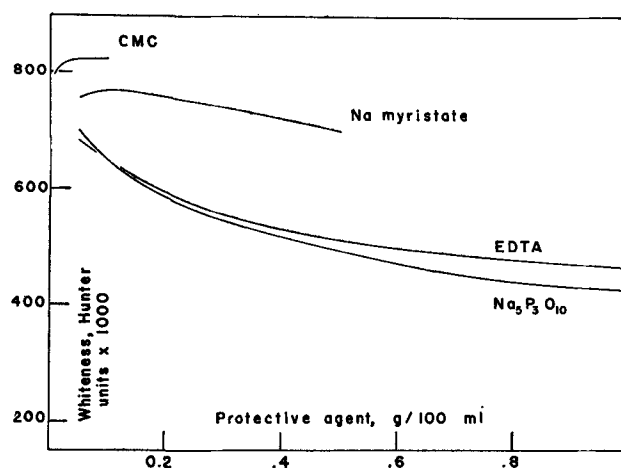

FIG. 10. Deposition at 120°F. in distilled water. The salt effect on a weight basis for sodium carboxymethyl cellulose, sodium myristate, tetra sodium ethylene diamine tetra acetate, and pentasodium triphosphate.

Conclusions

1. The common anionic detergent materials (alcohol sulfates, soaps MW 200-350) give a small but positive salt effect upon deposition of aquadag.

2. Chelating agents such as pentasodium triphosphate and tetrasodium ethylene diamine tetra-acetate suppress the effect of hard water ions by complexing and elimination of these ions from the system. However these protective agents introduce sensible

amounts of sodium ions. When these materials are used in hard water the observed minima in deposition (or maxima in whiteness of swatch) are a consequence of the stoichrometric titration to form the Ca or Mg complex followed by the normal increase in deposition due to added sodium ion.

3. Soaps remove divalent ion by precipitation, and thereafter the deposition due to salt effect is small.

4. CMC inhibits soil deposition in the presence of mono- as well as polyvalent ions. It does not sequester or remove calcium ion to any marked degree. The amount of CMC required for protection is relatively small.

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Panel on Drying Oils

I

Research, the Key to Future Markets for Drying Oils[1]

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UNDER A CONTRACT with the U. S. Department of Agriculture the Battelle Memorial Institute recently completed a year-long survey of the market potential for fats and oils in drying-oil uses. The report of this study will be published by the Department later this year or early in 1955. However John Cowan, of the Northern Utilization Research Branch, Agricultural Research Service, Peoria, Illinois, and Shelby Robert, of the Market Development Branch, Agricultural Marketing Service in Washington, under whose general direction this study was made, have given us permission to give you a preview of the report.

We feel that it is particularly appropriate for the initial report on this study to be presented before this Society. Several members contributed personally to the project by talking with us last winter and thus have a special concern with its outcome. All, we believe, will have an interest in the results because they bear rather closely on the future prospects of the industries that process and consume drying oils.

This study had its inception early in 1953. At that time the U. S. Department of Agriculture was becoming increasingly concerned by the sizable stocks of linseed oil in its custody, the decline in prices of most fats and oils, and the shrinking market for inedible fats and oils in drying-oil products. The Department was further concerned that the continuing shift by the using industries to petroleum derivatives, rubber-base paints, and synthetic resins in lieu of drying oils might portend a critical position for drying oils from agricultural sources.

Recognizing these problems, the Department outlined a study aimed at finding out a) the factors affecting the use of various fats and oils in the dry-

ing-oil industry, b) the difficulties being encountered by users of drying oils and the modifications desired to make the oils more useful in these industries, c) the reasons why synthetic materials, non-oil paints, and tall oil are capturing a larger share of the protective-coatings market, d) the price and supply conditions under which one drying oil might be substituted for another, and e) the present and probable future supply and price situation for materials used in the production of the synthetics which are replacing drying oils. It was felt that this information would put the Department and the drying-oil industry in a position to take more effective action, particularly in terms of marketing and technical research, toward maintaining or improving the position of agricultural drying oils in competition with non-fat products.

It should be apparent from this brief review of the objectives of the study that the primary aim of the project was to gather information and ideas that would ultimately benefit the farmer-producer of the crops from which drying oils are obtained. It necessarily follows however that any knowledge of how to process and use drying oils more effectively would also be of benefit to the industries that supply these oils or consume them in their manufacturing processes. It should further be pointed out that while our report suggests a general research approach that may help to overcome some of the problems of the drying-oil industry, it does not spell out the particular chemical or physical research techniques that should be employed. The determination of specific experimental techniques rests more properly with technical men who work with these oils in the laboratory the year around.

In setting up our survey, it was decided that personal interviews with key men from selected companies in the drying-oil industry would be the most effective method of gathering the needed information. In order to get a good cross section of opinion, interviews were sought and completed with 46 paint, var-