for this purpose is nordihydroguaiaretic acid. When this antioxidant is used together with phospholipid or citric acid, its effectiveness is enhanced. Addition of alpha-tocopherol to oils containing only traces of this antioxidant causes a significant increase in carotene stability, and its sparing effect on carotene *in vivo* (8) would further add to the desirability of its use in such oil solutions of carotene.

In refined cottonseed oil, carotene destruction occurred concurrently with the accumulation of peroxides. In the more saturated oils, carotene destruction occurred before much peroxide was detected in the oils.

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Synthetic Resins and the Drying Oils[1]

Some Aspects of Their Interrelation

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THE origin of the art of combining drying oils with resins appears to be lost in antiquity. Both components were natural products which were very little changed prior to use. Then, as later, it was recognized that films of hard resin were lacking in toughness and in flexibility and also that films of drying oils alone could be improved in brilliance and in the rapidity with which useful hardness was developed through the inclusion of resin.

While considerable improvement was made in the crushing and refining of the drying oils and in their heat processing, there was no basic change in the heat processing of the various oils and resins until recently. True, varnishes of widely different characteristics were obtained, but it may be argued that these characteristics were the rather mechanical averaging-out of the properties of the ingredients. It was not until the advent of the synthetic resins that in the field of air-drying coatings it became possible to add two and two and come out with five for an answer.

First came the rosin modified phenol-aldehyde resins. These, when properly combined with drying oils, gave a new order of speed to air-drying varnishes. When tung oil was employed, a useful increase in water resistance and chemical resistance was obtained. Certain types of these resins yielded varnishes with far less than the usual tendency to soften or sweat-back with age, a trying property shared by many of the natural oils and a few of the newer "synthetic" products. Following these rosin modified types came the 100% synthetic phenol-aldehyde resins. Many types were soon developed showing a very wide divergence as to their effect on the bodying rate of drying oils. The investigation of these differences and the comparison of the various types of phenolic resins against other classes makes a fascinating study. Unfortunately, it is far too involved a subject to consider here. Turkington and Allen (4) have described in detail the resin properties obtained through the use of the various substituted phenols. Shuey (2) compared a number of the phenol-aldehyde resins with other types in terms of their behavior with the various drying oils. In particular, the discussion bearing on the decreased oxygen intake of varnish films based on certain phenolic resins, the mechanism of the polymerization of these resins with oils and the effect of heat treatment and resin selection on both the application and service properties of the terminal varnishes merit close attention. In effect, the resin properties were added to the oil properties with a resultant good somewhat beyond their simple sum. This work, and that which will undoubtedly follow it, should give the oil chemist additional clues

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as to why the phenol-aldehyde resin-drying oil varnishes continue to be regarded as the most outstanding type for exterior durability, for chemical resistance, and for water resistance. Such clues, together with the rapidly increasing knowledge of the reactions of unsaturated fatty acids might readily lead to startling advances in the production of synthetic drying oils.

At the same time the phenol-aldehyde varnish resins were being developed, the type of synthetic resins which we know as "alkyd" came into general use. In this discussion only the vegetable oil modified types will be considered. It is significant that while for the main part the other air-drying coatings employed drying oils as such, the alkyds were essentially based on fatty acids. True, the fatty acids employed were generally simply the mixtures found in the natural oils since their separation was too costly to be commonly employed. The important difference was that the drying oil fatty acids and the natural glycerol split from them were being used as chemical reactants, built into a designed structure. Other reactants, both acidic and alcoholic, were likewise employed. Their selection was not haphazard, not because the ingredient grew there, but because its chemical configuration indicated the addition of useful properties. That the following of this line of reasoning is sound is shown by the fact that the alkyd type of resin has for several years sold in greater volume than any other type of synthetic resin used in surface coatings. So far almost complete commercial dependence has been placed on the drying oil fatty acids to supply the long unsaturated and conjugated chains needed. Whether this source will continue to be the one of major importance will undoubtedly depend to some extent upon the ability of the drying oil industry to furnish relatively pure fatty acids or their glycerides and to do so in competition with the chemical industry.

Before leaving the subject of alkyds, it would be well to consider briefly several types. Speaking loosely, within the paint and varnish industry, "alkyd" generally is taken to indicate the resins based on phthalic anhydride. This is understandable since the bulk of the tonnage is composed of this type. It is unfortunate, however, since it tends to limit a very useful generic term. Currently, a number of other anhydrides are being used with good commercial success. Maleic anhydride and fumaric anhydride serve a highly useful purpose, generally being used in conjunction with phthalic anhydride in order to supply additional reactivity where needed. Many of the more successful alkyds used in exacting industrial applications are so constituted.

Another, and possibly the most promising class of ester type resin, is that based on "Carbic" anhydride and generally marketed under the designation of the "C-9" resins. These differ profoundly from the phthalic alkyds and in ways which should be of interest to the drying oil industry.

The reactivity of phthalic alkyds, at least as relates to the formation of dry films, seems to derive from the complexity of the mixed ester produced during the formation of the resin and from the various reactions made possible by the unsaturation supplied by the fatty acid chains. In order to obtain the maximum speed of set and hardness of film the first of these factors must be very well developed. It follows that under these conditions the "resin" produced is essentially a finished vehicle, except for the possible device of blending with similar, or even quite different, vehicles. In any case, further processing with additional drying oil is not desirable. In fact, Jolly (1) has recently suggested that the dividing line between resin and varnish manufacture has been moved to such an extent that it might be better if the whole process were carried out under a single roof.

On the other hand, the "C-9" ester type resins based on "Carbic" anhydride exhibit an entirely different order of reactivity. The finished liquid resin may be further extended with drying oils and yet produce films of equivalent hardness and generally somewhat better through drying than phthalic alkyds which contain considerably less drying oil or drying oil fatty acids. A concrete example is the satisfactory performance of a 20-gallon "C-9" varnish (20 gallons of drying oil to 100 pounds of resin) in the vehicle chiefly used under Specification ES-680a. This is another way of saying that the drying oil has been greatly accelerated in drying rate; in fact, this effect is so pronounced that highly bodied varnish oils of 75 to 100 gallons in length, based on this same resin and linseed or soya bean oils, have been extensively used to replace faster drying oils in conventional varnishes. It is of interest in these days to the varnish-maker that the production of these varnish oils requires far less kettle time than would the oil alone. For example, we have the following comparisons:

75 gallons alkali refined linseed oil—100 pounds "C-9" resin.......	to Z-6 in 145 min.	to gel in 165 min. at 585°F.
Alkali refined linseed oil alone.......	to Z-6 in 350 min. at 585°F.	
25 gallons tung oil—100 pounds "C-9" resin....................................		to gel in 10 min. at 480°F.
Tung oil alone....................................		to gel in 27½ min. at 480°F.
"C-9" resin alone..........................		to gel in 16 min. at 480°F.

It is perhaps surprising that even with this acceleration of the bodying rate and drying rate of soft oils, the resultant films have remarkable flexibility. Even with linseed oil, a baked film on silk will retain its limpness after aging four years or more. Thus there is a type of mixed ester resin which is capable of being processed with various amounts of the several drying oils to produce a considerable variety of products in the conventional varnish equipment. With improvements in the drying oils or the better segregation of their components much improvement should be possible.

Recently the oil chemists have been making great strides in the preparation of "drying oil raw materials." Sorensen (3) made an admirable review of this in his paper on "Drying Oil Research" earlier this year. Most of the work listed there as being accomplished and all of the problems given as imperative are of vital interest to the resin manufacturers as well as to the resin user. It is certain that any advances towards cheap single drying oil fatty acids, or combining forms of similar functionality will greatly benefit the coatings industry of which we are all a part.

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Abstracts

Oils and Fats

Edited by
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FLAVORS IN FOOD FATS. H. E. Robinson and H. C. Black. *Ind. Eng. Chem. 37,* 217-19 (1945). Subject is discussed under title of rancidity, reversion and dietary effects of rancid fats. The section on reversion is of special interest because this is one of the few published descriptions of the phenomenon.

RATION BISCUITS. II. EFFECT OF TYPE AND CONCENTRATION OF SHORTENING ON KEEPING QUALITY. G. A. Grant, J. B. Marshall and W. H. White. *Can. J. Res. 23F,* 123-31 (1945). Ration biscuits prepd. by 2 manufacturers and contg. 8-23% of 1 compd. animal-vegetable and 3 all vegetable shortenings were stored at 43.3° for 36 wk. Keeping quality was assessed by flavour, peroxide oxygen, and pH detns. The type of shortening was found to have a greater effect on keeping quality than the fat concn. or plant practice. Biscuits made with stabilized hydrogenated vegetable shortening were more stable than biscuits made with a compd. animal-vegetable shortening. All biscuits became objectionable to the tasters after storage for 22 wk.

LARGE-SCALE PRODUCTION OF LIVER OILS FROM SOME NEW ZEALAND FISH. M. M. Cunningham and C. Scott. *New Zealand J. Sci. Tech. 26B,* 21-7 (1944). Two methods are described for the production of high- and low-potency liver oil. Fresh, high-potency livers were minced, boiled for 30 min. by steam, and centrifuged at 170-80°F. Fresh, low-potency livers were minded, added to an equal vol. of water and brought to a pH of 1.5-2.0 with 25% HCl. To this slurry was added com. pepsin in amt. equiv. to 0.05% of the fresh liver weight. The mixt. was maintained at a temp. of 110-20°F. and stirred constantly. At the end of 48 hrs., the batch was neutralized with Na_2CO_3, heated to 170-80°F. and centrifuged to remove the oil. (*Chem. Abs.*)

RETENTION OF THIAMINE, RIBOFLAVIN AND NIACIN IN DEEP FAT COOKING. G. J. Everson and A. H. Smith. *Science 101,* 338 (1945). Making allowance for the addn. of water to the dry mix in prepg. the dough and also for the fat absorbed during frying, it was found that the av. loss in thiamine during cooking was 22.9% and in niacin was 20%, whereas there was no measurable loss in riboflavin or in iron. It would appear, therefore, that the cooking in hot fat exerts a more deleterious effect upon this vitamin than does oven baking. The observation on the stability of riboflavin in the present study agrees with the published results of Andrews, Boyd and Terry on the stability of riboflavin during baking. As would be expected, no loss of iron could be demonstrated.

ADSORPTION SEPARATION IN THE FIELD OF FATS. V. THE SEPARATION OF CIS-TRANS ISOMERS. H. P. Kaufmann and W. Wolf. *Fette u. Seifen 50,* 519-21 (1943). Al_2O_3, SiO_2 gel and C were compared as adsorbents in the sepn. of an equi-mol. mixt. of tributyrin and tristearin. Tributyrin was more strongly adsorbed by Al_2O_3 and by SiO_2 gel and could be quantitatively sepd. Al_2O_3 or SiO_2 gel adsorbed mono-, di-, and tristearin in the order mono > di > tri. A mixt. of 1 g. each of the Me esters of fumaric and maleic acids in 35 cc. Et_2O was poured through a column of 25 g. C; 0.3 g. of the maleic acid ester was found in the filtrate. The "percolate" obtained with 35 cc. ice-cold Et_2O contained a mixt. of the 2 esters; 0.7 g. of the fumaric acid ester was obtained from the $CHCl_3$ eluate. A mixt. of 90% oleic, 10% elaidic acid was found in the eluate of the upper part of a SiO_2 gel column through which had been poured a C_6H_6 or petr. ether soln. of a mixt. of equal parts of the 2 acids. When the original mixt. was 80% oleic, 20% elaidic acid, the eluate contained 98% oleic acid; when the original mixt. was 90% oleic, 10% elaidic acid, pure oleic acid was sepd. With a mixt. of equal parts of brassidic and erucic acids in C_6H_6-petr. ether soln. and a C adsorbent, pure erucic acid was found in the filtrate. With a SiO_2 gel adsorbent, 60 to 100% of the erucic acid was found in the upper part of the column. (*Chem. Abs.*)

CONJUGATED UNSATURATED COMPOUNDS IN THE CHEMISTRY OF FATS. I. THE DETECTION OF CONJUGATED UNSATURATED FAT ACIDS BY MEANS OF THE TETRANITROMETHANE REACTION. H. P. Kaufmann and P. Kirsch. *Fette u. Seifen 50,* 314-16 (1943). Fats and fat acids contg. double bonds give intense red colors with $C(NO_2)_4$; nonconjugated unsatd. compds. give yellow colors. The intensity of the red color is much greater with 3 than with 2 conjugated double bonds. Tung oil, oiticica oil, parinarium and trichosanthes oil give a reddish yellow color in a diln. of 1:1000. The test can be carried out by adding 0.2 cc. $C(NO_2)_4$ to 0.5 g. oil or fat acid in 0.5 g. $CHCl_3$, and further dilg. with $CHCl_3$ if the color is too dark. (*Chem. Abs.*)

TESTS FOR PURITY OF OLIVE OIL. J. S. Gerona. *Mon. farm. 50,* 363-5 (1944). Wash the oil with a quantity of NaOH in EtOH, calcd. from the detd. acidity of the oil, filter and decolorize with animal charcoal or fuller's earth and filter again. Pour over the oil in a test tube a layer of trichloroacetic acid liquefied with 8% H_2O. A fine gray film developing at the surface of contact within 1 hr. indicates a refined olive oil. A gray-bluish or green film indicates nat-