TABLE IV

Carry-through Activity of BHA-Tocopherol Combinations

Antioxidant	AOM Stability (hrs.)	Oven Stability at 63°C. (hrs.)		
		Crackers	Pastry	Potato Chips
Control lard	7	163	307	67
Tocopherol[a] 0.01%	29	288	518	566
Tocopherol 0.05%	27	984	1339	2045
Tocopherol 0.10%	23	1497	1747	2496
BHA 0.01%	31	1044	1805	1133
Tocopherol 0.01% BHA 0.01%	33½	798	2006	1709
Tocopherol 0.05% BHA 0.01%	27	1257	2370	2473
Tocopherol 0.10% BHA 0.01%	24	1680	2342	2781

[a] Supplied by a concentrate containing 30% tocopherols, mostly gamma.

The maximum AOM stability was provided by 0.01% tocopherols in one lard and by 0.05% in the other lard. Increasing the concentration of tocopherols then provided less stability in conformance with the observations of other workers, as noted above. The maximum stability provided by the combination with BHA resulted from use of 0.01% tocopherols, and when increased levels of tocopherols were used, a decreased stability resulted. The presence of BHA did not prevent the pro-oxidant effect of the higher levels of tocopherols. There was no positive synergistic activity between antioxidants in either lard.

The carry-through tests revealed a different situation. The higher levels of tocopherols provided increased oven stability in all test foods. The higher levels of tocopherols in combination with BHA provided a further increase in oven stability. The combinations with BHA provided greater stability than the corresponding level of tocopherol used alone. Generally the combination of 0.01% tocopherols with 0.01% BHA provided better carry-through stability than BHA used alone at 0.01%. It was observed in lards and foods made with lard containing 0.05% and 0.1% tocopherols that a pronounced off-flavor, described as fishy, was developed.

The reasons for the increased carry-through activity with higher levels of tocopherols are not clearly apparent. Perhaps the heat treatment involved in cooking may destroy or modify tocopherols to a level where they do not exert the pro-oxidant effect. There is also the possibility that the function of the tocopherols is altered in the complex system of a food so that the effect is reversed.

These studies indicate that tocopherols are indeed carry-through antioxidants. It is implied that improved stability of foods made with fats containing tocopherols can be accomplished by the use of BHA although the AOM stability of the fat may not be improved significantly.

Studies designed to test the effectiveness of tocopherols with other antioxidants revealed a negative synergistic effect with all tested except BHT. The antioxidant effect with BHT seemed to be merely additive. The antioxidants showing a negative synergism under conditions of the AOM test with the tocopherol concentrate in lard were BHA, nordihydroguariaretic acid, diphenyl-p-phenylenediamine, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, and p-hydroxydiphenylamine.

Acknowledgment

Data for the studies reported have been accumulated gradually over a period of several years and have involved the efforts of several people. Grateful acknowledgment is made for the efforts of Lotte Marx, Elaine Josephson, Patricia Bristow, and Eugenia Hoffert.

The tocopherols used in these studies were furnished through the courtesy of Norris D. Embree of Distillation Products Inc.

Summary

1. Tocopherols have been found to be carry-through antioxidants in lard.
2. Gamma tocopherol, which is a better antioxidant than alpha tocopherol, is also a better carry-through antioxidant.
3. Higher levels of tocopherol provide increased carry-through stability although the AOM stability of lard is decreased.
4. Combinations of BHA with tocopherol in lard provide increased carry-through stability but do not increase the AOM stability.

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[Received May 24, 1956]

New Integrated Refining Process for Edible Oils[1]

G. C. CAVANAGH, *Ranchers Cotton Oil, Fresno, California*

SINCE JANUARY, 1950, at least 30 papers have been presented before this Society or in the Journal of the American Oil Chemists' Society dealing with the problems and virtues of recovering oil from vegetable and animal source material by means of solvents. This attests to the considerable interest shown by the industry in this type of oil recovery. For a number of years the research facilities of Ranchers Cotton Oil have concentrated on solving some of the problems associated with this type of operation.

One of the major problems encountered in a solvent type of operation is buyer resistance to dusty solvent meal. The desirable economic factor of an additional 20 to 50 lbs. of oil per ton of vegetable source material processed is in part offset by a meal that is difficult to sell in competition with Expeller or hydraulic pressed meal which contains 2% to 4% more oil.

We have successfully resolved the dusty meal prob-

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[1] Presented before the Spring Meeting of the American Oil Chemists' Society in Houston, Tex., April 22–25, 1956.

lem in the following manner. First, it was established that phosphatides, fatty acids, soaps of fatty acids, and other components such as pigments naturally occurring in the source material could be removed from the oil and redeposited on the meal with decidedly beneficial results. This was subsequently pointed out in papers by Pons, Thurber, and Hoffpauir (1), also by Chang, Couch, and Lyman (2). Our treated meal was compared with meals from other prepress-solvent plants throughout the country. Meal and oil from our plant was variously identified in these papers as 6, 6A, 6B, 6C. We have now standardized our plant production to correspond with meal 6A reported in the paper of Chang *et al.* This meal is produced by flaking the meats in five high rolls to 0.015 in., followed by cooking in five high stack cookers.

The meats are discharged from the cookers at 214° F., with 8 to 10% moisture. Granular soda ash is added to the wet cooked meats at a rate sufficient to precipitate the phosphatides and control the FFA of the crude oil produced within desired limits. We maintain a pH somewhat below the pH obtained by King *et al.* (3) in their special wet alkali cooks (4, 5).

By a series of screening tests comparing our soda ash, foots-treated meal with other solvent meals we determined that, unlike the other meals tested, our treated meal was not dusty until it had been ground in an attrition or hammer mill. To overcome this objectionable characteristic our treated meal is now screened. Only the particles passing over the 20-mesh perforations on the screen are ground in a horizontal hammer mill and blended with the meal which passes through the screens. A dust-free meal satisfactory for pelleting, feeding directly to livestock, or for formulating mixed feeds is produced in this manner.

The next problem resolved is indirectly connected with meal quality but specifically deals with the problem of carbonaceous and gummy deposits in the solvent recovery system and in crude oil storage tanks. It was determined that n-hexane dissolved gums, waxes, and possibly some pentoses from the meats and/or hulls. This material was observed to deposit in the stills and storage tanks both before and after the soda ash treatment described above. Residual moisture of .02 to 0.1% from the final steam-stripping of the crude oil was found to be the cause of the degumming. The result was dirty distillation equipment and gummy deposits in crude oil storage tanks, necessitating frequent cleaning and maintenance shut-downs. Obviously if the miscella were refined before recovering the solvent in the stills, both problems would be solved. Further laboratory investigation showed that both air (oxygen) and light have a deleterious effect on both crude oil and/or crude miscella. Removal of the light and oxygen sensitive components by refining as soon as possible after separating the oil from the source material produced an oil of great color and flavor stability (1). These observations led to an investigation of miscella refining.

CERTAIN ADVANTAGES of miscella refining are apparent from recent literature (6, 7, 8). An absolute viscosity of 3.1 lbs./ft./hr. at 100°F. with 40% cottonseed oil in n-hexane as compared at 83 lbs./ft./hr. at 100°F. for 100% cottonseed oil indicates greatly improved flow characteristics in favor of the miscella. To a refiner this means more pounds of oil per centrifuge per unit of time. It also means more rapid and efficient clarification of the soap from the refined miscella and more efficient removal of the oil from the soapstock. The net result is lower refining loss or more pounds of refined oil per unit of crude oil.

Our investigation of publications and patent literature indicated that miscella refining had not been practical because of the difficulty of color removal and necessity of controlling the concentration of oil in miscella within narrow limits. We have been able to overcome both of these objections. Others have obtained patents on miscella refining, based on the assumption that color removal at less than 65% concentration of oil in miscella was difficult or impossible (9, 10). This is not in accordance with our findings.

In our prepress-solvent operation the filtered prepressed oil is blended with the filtered 20% miscella from the extractor. The resultant miscella is approximately 40% by weight of oil. Miscella from straight solvent-extraction operations averaging 19% concentration has been successfully refined to very low bleach color (1.4 Red/14 Yellow) Lovibond and refining losses 10% above the Wesson loss of the crude oil. However the size of the refining equipment necessary to process large volumes of miscella for small yields of oil make this type of refining seem uneconomical. Concentration to approximately 40% oil would be a practical solution to this problem.

To insure constant concentration during refining operations, miscella is constantly mixed by circulating pumps in mixing tanks of sufficient size to run the refinery for 4 to 8 hrs. Two of these tanks make continuous operation possible. Pretreatment of the cooked meats allow lye solutions of 6 to 12% NaOH to be employed in this miscella refinery. Controls are simple, and centrifugal separation is efficient. The control panel for an entire miscella refinery consists of three flow meters: one for crude miscella, one for weak lye solution, and one for refined miscella wash water.

Based on several years' plant operation, we found the average moisture and volatile matter in our miscella refined soapstock to be 76%; 83% of the M & V is water and 17% is solvent. If we consider that the specific gravity of conventional caustic soapstock is 1.1000 and the composition of conventional caustic and miscella caustic soapstocks is identical except for the 12.92% of hexane in the miscella caustic soapstock, then the specific gravity of miscella caustic soapstock becomes 1.0457. The specific gravity of pure cottonseed oil at 100°F. is 0.9075 while the specific gravity of 40% cottonseed oil in n-hexane at 100°F. is 0.7528.

TABLE I

Oil Yields and Refining Methods Compared

	100% Cottonseed Oil Conventional Caustic Refining from Expeller Operation	40% Cottonseed Oil in n-Hexane, Solvent-Extracted-Miscella Refined
Oil in Seed	20%	20%
Total Oil per Ton Seed Clean Basis	400 lbs./ton	400 lbs./ton
Oil Lost in Hulls	3 lbs.	3 lbs.
Oil Lost in Meal	36 lbs.	9 lbs.
Total Oil Lost in Meal and Hulls	39 lbs.	12 lbs.
Total Crude Oil Available	361 lbs./ton	388 lbs./ton
Actual Refining Loss	4.39%	3.61%
Actual Pounds of Oil Lost Refining	15.8 lbs./ton	14.0 lbs./ton
Yield of Refined Oil	345.2 lbs./ton	374 lbs./ton
Oil in Soap (Dry Basis)	21%	12%
Absolute Viscosity @ 100°F	83 lbs./ft./hr.	3.1 lbs./ft./hr.
Specific Gravity @ 100°F	0.9075	0.7528
Sp. Gr. Soap @ 100°F	1.1000	1.0457
Bleach Color (Lovibond)	2.3 red/20 yellow	1.4 red/14 yellow

These data point up the advantage of lower viscosity and greater difference between the specific gravity of the soapstock and the refined miscella that work in the refiner's favor to reduce refining losses in miscella refining. This is accomplished mainly by using weak lye solutions not exceeding 12% NaOH by weight, and by producing soapstock low in free oil compared to conventional refining, where the free oil in soapstock on a dry basis is frequently as much as 40% (11). The free oil on a dry basis in our miscella refined soapstock has averaged 12%, and actual plant refining losses have averaged 3.6% over a long period on California cottonseed oil. In our particular area the saving due to lower free oil in soapstock amounted to approximately two pounds of refined oil per ton of cottonseed processed when conventional caustic and miscella refining were compared.

It should be emphasized that the data included in this report are based on actual operations with California crude cottonseed oil. Variations in refining loss and refining characteristics of cottonseed oil have been observed to change from season to season on the same variety of seed in the same locality. These variations are usually small compared to the differences in refining characteristics of crude vegetable oils produced in different sections of the country. This is pointed out to emphasize the difficulty in evaluating the efficiency of various refining processes on different types of crude oil. Guarantees have been made on refining processes for a certain percentage gain over the American Oil Chemists' Society cup or settlement loss. We believe a large gain over cup loss is either an admission on the part of the crude oil producer that the extraction or pressing plant is not operating efficiently or that a well-processed crude oil has deteriorated between its point of origin and place of processing. It does not necessarily follow that one particular oil recovery and refining process is more efficient than another as the percentage gain over the cup loss increases. In our oil recovery and refining process at the oil mill level the closer the actual refinery loss approaches the cup loss, the more efficient the refining process becomes. A well-processed crude oil in our integrated refining operation will show little difference between cup loss, Wesson loss, chromatographic loss, and actual refinery plant loss. Integrated refining at the oil mill level emphasizes producing the maximum pounds of refined oil per ton of source material rather than in producing the maximum amount of refined oil per tank car of crude oil.

The water-washed miscella from the secondary centrifuges in our refinery was found to contain from 0 to 2 ppm. of soap by our method of analysis,[2] and an average bleach color of 1.4 Red/14 Yellow when the solvent was removed. Bench-scale studies in a quick-freeze cold-storage plant indicated that well refined miscella could be winterized in commercial hexane. We found an 85% yield of wintered oil with at least 15-hr. chill test could be obtained in four hours. These data are in disagreement with the conclusions reached by Boucher and Skau in their phase relations work (12).

A plant which is now in continuous operation was constructed on the basis of bench-scale and pilot-plant data. Plant yields and chill tests are comparable to or better than conventionally winterized California cottonseed oil. The miscella winterized oil requires only 1/18th as long to produce as conventionally winterized oil.

After miscella refining and winterizing the stearines and winterized miscella are continuously separated in a settling tank. The stearines are drawn from the bottom of the tank through an indicating flow-meter. The winterized miscella is decanted from the top of the separating vessel. The costly and time-consuming steps of filtering are completely eliminated. Both the stearines and the winterized oil are recovered from their respective miscellas in separate solvent-recovery systems. The stearines are cooled and sent directly to storage. The winterized oil is pumped through Dowtherm heat-exchange equipment into a continuous deoderizer of our own design. The volatile components are steam-distilled from the oil. The deodorized oil is cooled at 110°F. and saturated with nitrogen as it is pumped to storage.

A full-scale plant is now in operation at Ranchers Cotton Oil, Fresno, Calif., continuously miscella-refining, solvent-winterizing, and deodorizing 80,000 lbs. of cottonseed oil per 24 hrs. We believe this to be the only integrated oil-processing plant in existence at this time. The total elapsed time from seed in storage to nitrogen-protected salad oil in storage is 18 hrs. The additional labor required in converting from an 80,000-lb. per day crude cottonseed-oil plant to a salad-oil plant of the same capacity is one man per shift; this man is in the solvent plant. Laboratory control in this type of operation must be more elaborate than is normal for conventional crude-oil mill operation but not as elaborate as a conventional salad-oil plant. By controlling the unit processes from conditioning the seed in storage throughout the entire operation to the salad oil, we are able to take some of the variables and undesirable characteristics out of the oil, which cause reversion problems in conventionally refined oils. The net result is a salad oil with a bland flavor, light color, and exceptional keeping qualities.

Tank car or tank truck lots of salad oil produced in and shipped from our plant have had the following average analysis:

Color	2.2 red/20 yellow (Lovibond)
F.F.A.	0.02% (or less)
Peroxide Value	0 to 0.3 milliequiv./1,000 g.
Soap	0 to 2 p.p.m. (by our method of analysis)
A.O.M.	18+ hrs. (without added antioxidant)

Summary

Dust-free solvent meal can be produced by pretreating meats with granular soda ash prior to oil extraction, addition of foots from miscella-refining operation to meal, and screening meal from dryers prior to grinding, then grinding only overs and blending with screened meal.

By exclusion of air and light and by properly coordinating the miscella refining procedure, light-colored, soap-free oil can be produced, using low Baumé lye.

Refined miscella can be winterized in a short enough time to warrant doing it in a continuous plant, giving yields and chill tests comparable to or better than conventionally winterized oil.

A continuous deodorizer followed by continuous injection of nitrogen into the deodorized, cooled salad oil protects the oil from oxidation in this integrated, continuous salad-oil plant.

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[2] Soap is extracted from oil with 2% aqueous-acetone mixture and titrated with 0.01 nHCl, using bromphenol blue as indicator.

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[Received May 7, 1956]

The Kinetics of the Hydrogenation of Pure Fatty Esters. II. Mono-olefinic Systems: Cis-trans Isomerism

FRANZ A. VANDENHEUVEL, Fisheries Research Board of Canada,
Technological Station, Halifax, N. S., Canada

THE FORMATION of *trans* isomers in the course of hydrogenation is considered a phenomenon of considerable importance to the commercial hardening of oils. It would seem desirable therefore, from a practical as well as from a theoretical standpoint, to obtain a satisfactory picture of the mechanism underlying *cis-trans* isomerism.

The contribution of Feuge *et al.* (2) toward a solution to this problem is important for several reasons, in particular, in supplying reliable data through the use of an infrared spectrophotometric method established by Swern and co-workers (4). These data show many points of similarity between the behavior of triolein and that of methyl oleate over a wide range of conditions. One of the salient features of the reaction, as revealed by this study, is the gradual evolution of the system toward a *cis-trans* equilibrium. Another feature is the necessity of the presence of hydrogen for the formation of *trans* isomers, in contrast with *cis-trans* isomerization reactions, such as those promoted by selenium. A possible explanation is that the adsorbed complex formed from hydrogen, nickel, and the unsaturated compound is the origin of both the saturated compound and the isomeric unsaturated form. It is probable that a certain proportion of the complex units, instead of being released from the catalyst in the form of saturated molecules, break down and revert to the constituents. Unsaturated constituents so released could be either *cis* or *trans* if the structure of the complex were such as to allow free rotation between the carbon atoms originally linked by a double bond. It is one of the purposes of the present article to show that the above postulate is consistent with hydrogenation data. For this purpose, data which Swicklik *et al.* tabulated in a recent article (3) will be used.

These authors have carried out experiments similar to those of Feuge *et al.* with a view to checking a postulated mechanism of the reaction. They concluded that a true first order model for the reactions involved was incompatible with the data. Good agreement was obtained when all rate constants were multiplied by the same function, $1 + at$, indicating, in their opinion, that the effectiveness of the catalyst increased with time. In their experiment No. 2, for example, the effectiveness of the catalyst would have increased four times by the end of the reaction. This would seem difficult to reconcile with the fact that the over-all hydrogenation rate was very constant throughout. It is another purpose of the present article to explain this and other puzzling facts, using to this end conclusions relative to zero order hydrogenation kinetics enunciated in Part I of the present series (5).

It is probable that a systematic study of the reaction by the method initiated by Feuge *et al.* will ultimately provide considerable help to the technologist by removing much empiricism from commercial hydrogenation practice. This would result from a comparison of reaction rate constants under various conditions. A simple method for the computation of these rate constants is given below.

Proposed Mechanism

Figure 1 describes the various phases of the reaction involving a system initially composed of a *cis* mono-olefinic ester, a nickel catalyst, and hydrogen. The temperature is assumed high enough to promote formation of *trans* isomers. Double bond shifts also occur, but adsorptive and reactional behaviors are assumed to be identical for all forms which are geometrical homologues. Thus $\bar{A}$ represents all the *cis* and $\bar{B}$ all the *trans* homologues.

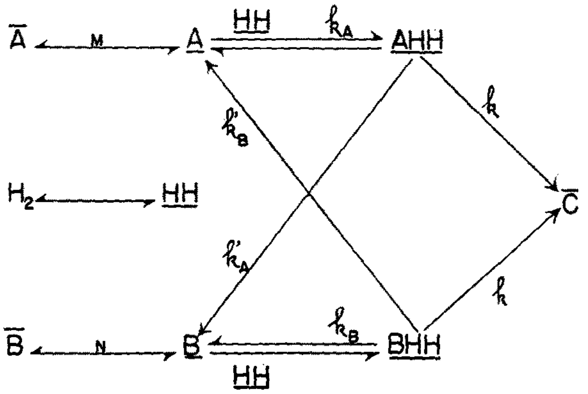

FIG. 1. Diagram describing a mechanism proposed for the hydrogenation of methyl oleate or triolein in the presence of a nickel catalyst.