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Developments in the Refining of Oils With Sodium Carbonate

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SEVERAL years have elapsed since the writer described the Clayton Soda Ash Refining Process (1). The purpose of this paper is to review some of the developments that have since been made in refining fatty oils with sodium carbonate. The desirable properties that sodium carbonate has of neutralizing the free fatty acids without appreciable attack on the triglycerides under refining temperatures and the relatively low cost of this chemical were well known. But the evolution of carbon dioxide from the reaction of sodium carbonate with the free fatty acids resulted in persistent emulsions and floating soapstock. A method that would successfully employ sodium carbonate for refining oil with separation into clean oil and low free oil soapstock remained a challenge. It was not until the Clayton process in which the dehydration-rehydration sequence was employed that the problem may be said to have been solved in a practical manner. It is not within the scope of this paper to go into details of equipment for carrying out the process or to refer to and describe the layout of installations that have been made. The discussion will be confined to certain chemical aspects of the refining at different stages. The process, as carried out in practice is stream lined and continuous. Units of one- to four-tankcar a day capacity have been in operation for the past few years. The essential components of the process will be described in condensed fashion. A complete account of it has been published (1).

The neutralizing sodium carbonate solution 20° Bé. in excess, usually 1.5 times that required to combine with the free fatty acids, is added to the flow of crude oil. The mixture is heated to 190-212°F. before it is introduced into a vessel, a dehydrator, maintained under a vacuum, where the water is flashed off and

any gases released. With crudes of a high per cent of gums or a high ratio of gums to F.F.A., a larger excess of sodium carbonate is recommended. The oil and dehydrated soapstock are pumped from the dehydrator and rehydrated with sodium carbonate solution. The amount employed on the average will vary from 2 to 7% of a 20° Bé. solution with the most common 3 to 4%. The sodium carbonate does not attack the oil to a measurable extent under these conditions and because of the high concentration of electrolyte prevents the formation of stable emulsions. Separation of the soapstock from the oil takes place readily in the centrifugal. The degree of fluidity of the discharging soapstock may be controlled and regulated by adjusting the amount of rehydration solution added. It is found advisable in most cases to maintain the soapstock at a level of 33 to 35% water, which is close to that of the water content of neat soap.

The sodium carbonate solution may be added in two streams for rehydration, one 20° Bé. injected into the dehydrated soapstock-oil mixture as it leaves the dehydrator, and the other, 12° Bé. to the soapstock in the centrifugal. In this way, for certain oils high in gums, some economy in sodium carbonate consumption may be effected. The first sodium carbonate solution for rehydration is added in an amount not quite sufficient to cause the soapstock to slide out of the centrifugal and be discharged readily. The second stream is regulated to that quantity that will result in the the uniform discharge of the soapstock. One of the important points in this type of operation is to have the sodium carbonate stream to the centrifugal below a given concentration, i.e., specific gravity, otherwise uneven discharge of the effluents occurs. Some soapstock begins to come over with the oil. This hap-

pens when the solution is 20° Bé. and does not take place when the solution is 12° Bé. If one were to hazard an explanation, one would be inclined to say that the solution of lower concentration mixed with the soapstock separating near the bowl wall because the specific gravities of the two were not too far apart, whereas the solution of higher concentration found its way to the bowl walls without mixing sufficiently with the soapstock. This created an imbalance, and before long the oil began to discharge dirty. The divided streams method of treating the dehydrated mixture is illustrated to show the many variations that are possible and would be indicated only in cases where there was an inordinately high consumption of sodium carbonate required to push out a very stiff soapstock. It also affords some insight into the mechanism of the action of the flush to the soapstock in the bowl.

THERE are some interesting differences between the soapstocks from sodium hydroxide and sodium carbonate refining of crude fatty oils. Sodium carbonate appears to form some complex with the phosphatides which does not degrade or decompose as readily as the corresponding sodium hydroxide combination. The difference in behavior of these complexes or salts shows up strikingly in their solubility in petroleum ether. When soda ash soapstock, cottonseed soda ash soapstock for example, is extracted directly with this solvent, the extract after evaporation is a semi-solid mass which is high in phosphorus. Under the same conditions of extraction, sodium hydroxide soapstock yields an oil relatively devoid of phosphorus.

To avoid the inclusion of the phosphatide and other gum complexes in the "free oil" of sodium carbonate soapstock it is dried, and the dried soapstock extracted with acetone in which the oil is soluble but the phosphatides and the phosphatide complex are not. The phosphatide-complex with sodium carbonate behaves like phosphatides in that an oil is recovered when the petroleum ether extract, dried, is extracted with acetone. The phosphatides remain insoluble. These observations were made the basis of a method for the determination of "free oil" in sodium carbonate soapstock.

Another anomaly of sodium carbonate refining by the Clayton soda ash process, which is the dehydration-rehydration sequence, followed by a caustic wash, is the lower final bleach color of cottonseed oil than the cup even when the refined oil color is higher than the cup color. This is of practical importance since it means a saving in the bleaching agent required and a corresponding reduction in the loss of adsorbed oil.

With the increased interest in and importance of fat-soluble vitamins, which are associated with the unsaponifiable matter of fatty oils, methods were devised for their isolation and differentiation. Although Jamieson (2) records a range of values for unsaponifiabiles in crude and in sodium hydroxide refined cottonseed oils, for example, 0.9 to 2.0% for the former and 0.7 to 1.5% for the latter, it was not commonly realized by those concerned primarily with the refining of oils that a significant proportion of the unsaponifiabiles was removed in refining with alkali. Von Fellenberg (3) reported 1.65 to 1.83% for the unsaponifiabiles of crude and 0.98% for that of refined rape oil.

There have been some disclosures of methods of obtaining unsaponifiabiles from oil and soapstock sources. Kruse *et al.* (4) neutralized crude fatty oils with sodium hydroxide solution in the presence of a filter aid and then extracted the latter with acetone. Extracts of 2.0 to 10.0% sterols were reported. Hickman and his co-workers have utilized crude fatty oils as a source of tocopherols. The oils are subjected to a very high vacuum in a specially designed molecular still. A distillate with a high concentration of tocopherols is produced. It has been customary to follow the course of refining in terms of F.F.A. and color. With the introduction of degumming, the growth of which was stimulated by the practical and efficient process that Thurman (5) developed, more attention is being paid to the phosphorus of the crude and the degummed oils. But as a rule, little has been revealed concerning the distribution of the other so-called minor constituents in the refining operation.

Crude oil may be considered a mixture of several different species, each with its individual solubility in the oil. It is, therefore, possible theoretically to devise methods for removing one species in a higher concentration than another, through the proper choice of a selective solvent or specific adsorbent. Phosphatides are soluble in oil but in the presence of water become hydrated and insoluble. The precipitated hydrated phosphatides have more unsaponifiable matter than the crude oil from which they are derived. As will be brought out later, the degree of phosphorus removal reflects to a large extent the degree of refining, that is, the removal of the other concomitant impurities.

IT was thought that there might be differences between sodium hydroxide and sodium carbonate refined oils with respect to the unsaponifiabiles in them. Analysis of an oil discharged from the primaries of the sodium carbonate process and an oil from a continuous sodium hydroxide refining revealed differences in unsaponifiabiles. When a comparison of the unsaponifiabiles of corn, cottonseed, and peanut oils that were sodium carbonate and sodium hydroxide refined was made, the magnitude of the difference was 0.1 to 0.4%, the sodium carbonate refined oil having values higher than the same oil sodium hydroxide refined. The oils showed a similar difference in vitamin E, alpha tocopherol determined by the Emmerie-Engel technique. Sodium carbonate refined oils retained about twice as much alpha tocopherol as the sodium hydroxide refined oils investigated.

It was reasoned that since there were more unsaponifiabiles left in a sodium carbonate than in a sodium hydroxide refined oil that as between the two the former would yield concentrates higher in unsaponifiabiles. This was found to be the case when the caustic soapstock of sodium carbonate refined oil was dried and the acetone extract analyzed for unsaponifiabiles (6). The extract assayed very high in unsaponifiabiles, 78 to 85%. The gums having been almost completely removed, the free fatty acids reduced to about 0.03% and the color taken out for the greater part, the soda ash neutralized oil is, therefore, a unique source for the production of an extract high in unsaponifiabiles. The soapstock from the caustic wash step may be dried before extraction with a solvent such as acetone that dissolves the unsaponifiabiles and not soap. Or the soapstock may be acidu-

lated to break out a fatty layer that contains the unsaponifiables.

The concentration of unsaponifiables appears to be selective, that is to say a greater proportion of one class or type is removed or adsorbed in the caustic wash than others. For example, a crude soya bean oil assaying three micrograms of carotin per gram of oil, 0.0003% carotin, when soda ash refined and the neutralized oil then caustic washed gave a soapstock, which when dried and extracted with acetone yielded, in turn, a residue that contained 2.3% carotin—a concentration of 7,600 compared to that of the crude oil. The recovery of carotin in this caustic wash step was 60% of that present in the original crude oil. The refining soapstocks are however, not the most efficient adsorbents of the unsaponifiables of crude oil since, as was remarked before, they do not remove a major proportion of the total unsaponifiables.

Alpha tocopherol likewise was found to be concentrated in the acetone extract of the dried caustic wash soapstock from sodium carbonate refined soya bean oil. In one instance, a 2% alpha tocopherol extract was obtained from the caustic wash soapstock—a 10-fold concentration over that in the original crude oil. But the yield referred to the tocopherol of the crude oil was very low, a fraction of a per cent. This was in a measure due to some tocopherol having been removed in the soda ash refining, the acetone extract of the dried soapstock from which had 1% tocopherol which represented only 3% of that in the original crude oil. The caustic wash soapstock offers a better source for a purer product because of the absence of appreciable free oil, gums, and other impurities and much lower per cent of soapstock, dry basis, compared with the sodium carbonate soapstock.

It is not the intention on this occasion to view these phenomena from the standpoint of any immediate economic potentialities of sodium carbonate and caustic wash soapstocks as sources of tocopherol, carotin, and other vitamin-like products but rather to present data that may lead to a fresh approach to the examination of the streams from the refining of oil. In the future it may be surmised that there will be more to refining of oil than just adding alkali to crude oil to produce refined oil and soapstock, the latter to be converted to black grease or to find its way to the soap kettle.

Refining—The Caustic Wash

The oil leaving the primary centrifugals of the sodium carbonate process is neutralized and refined, but most cottonseed oils require treatment with sodium hydroxide solution further to reduce the color. Concentrated sodium hydroxide solution, 20° Bé. solution for example, attacks the color bodies and residual phosphorus-containing substances without appreciable attack on the oil when the over-all process is rapid. But when the mixture is separated in a centrifugal, the means now almost universally practised in oil refining plants for the separation of soapstock from oil, stratification occurs, that is, the soap is salted out. The result is a fractionation of the mixture into three phases, a dark colored niger, the heaviest phase, an intermediate soap layer, and an oil layer. Before long, the soap phase begins to come out with the oil, or the oil may break over into the soapstock. A clean separation in the centrifugal does not take place. The problem of employing 20° Bé. sodium hydroxide solu-

tion and still obtaining a clean, efficient separation in the centrifugal was solved in a rather simple and ingenious way (7). A stream of water was directed to the soapstock being separated within the centrifugal. The water does not mix with the feed of oil-soapstock mixture but contacts the soapstock exclusively, so to speak. Hot water is introduced into the centrifugal through a pipe. The water follows a confined path separate from the feed and the oil and exits from the pipe at a point close to the bowl wall. The soapstock is diluted to such an extent that the soap is no longer salted out. Fractionation is thus overcome in the area where it begins to be accentuated in the centrifugal. Instead of oil containing fractionated soap, the oil discharge is clear and the soapstock is a dark-colored liquid. As long as the water flush is made available continuously to the soapstock in the centrifugal in the manner indicated, the oil will continue clean. The extent of dilution is dependent on the initial concentration of the sodium hydroxide and the amount of impurities in the oil. It may be expressed in terms of the concentration below which the sodium hydroxide of the soapstock must be reduced in order to overcome or prevent stratification. The value is usually less than 8° Bé. NaOH. In practice the diluting water is 10 to 20% of the oil feed.

This method of treatment may be applied to the refining of several types of oil which are characterized by low impurities as well as to sodium carbonate refined oil. In both, the oil can be treated with sodium hydroxide solutions of high concentration to get the benefit of the thorough-going attack of this reagent on the impurities without fear of significant loss of oil through saponification, and by employing the expedient of a flush to the soapstock in the centrifugal avoid appreciable loss of oil through entrainment. The refining losses incurred are of the order of 0.1 to 0.25% depending on the amount of impurities present in the oil.

The scheme permits the "safe" contacting of the appropriate oil with concentrated sodium hydroxide, 20° Bé. and higher, which act more effectively on the color bodies, phosphorus compounds, and residual acidity than less concentrated solutions. Sodium carbonate refined oils that are caustic washed with 20° Bé. solution with a flush to the centrifugal, the oil then being immediately water washed as is common practice, yield oils that are thoroughly refined when measured not only by the color and acidity but also by the phosphorus that remains. Oils so processed have ½ p.p.m. and less of phosphorus. The low phosphorus of itself is as much an index of a thorough refining at this stage as it is a practical measure of the extent to which other impurities have been correspondingly exhausted from the oil. In other words, if the phosphorus of an oil has been reduced to below a given low figure previously established for good quality refining after a caustic wash, it can be reasonably assumed that the color and acidity will have been reduced concomitantly in a related manner.

Although there is little direct evidence that the phosphatides and phosphorus containing substances and the color bodies are linked together in some crude oils, the color and phosphorus of partially and "thoroughly" decolorized oils appear to be inter-related. That is to say, as the color is removed, so is the phosphorus. It may be remarked, in passing, that the phosphorus of an alkali refined oil is prob-

ably present not as a phosphatide but as some other compound or compounds as yet not identified. It is also interesting to note that the ratio of phosphorus to nitrogen of an alkali refined oil is different from that of the crude oil. The determination of nitrogen in oils in p.p.m. leaves much to be desired. The degree of alkali refining may be inferred from the phosphorus of the oil.

In conclusion, it may be remarked that the performance of the Clayton Sodium Carbonate Refining Process in practise during the past few years has been

such as to justify the use of the Wesson Absolute Refining Loss as a yardstick with which to compare plant refining losses, proposed when the process was first introduced.

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Colorimetric and Potentiometric Determination of Acid Numbers of Vegetable and Marine Oils¹

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A COLORIMETRIC method for the determination of acid numbers has been developed, utilizing isopropanol-benzene as the titration solvent and offering several advantages over either of the present A.S.T.M. or A.O.C.S. colorimetric methods. The A.S.T.M. potentiometric method has been satisfactorily applied to vegetable and marine oils, particularly to dark or colored oils. Close correlation was found between the acid numbers obtained by these two procedures, making it possible to compare directly colorimetric and potentiometric results. It is suggested that these two procedures be investigated for possible adoption as A.O.C.S. Official Methods.

Methods for the determination of acid numbers in petroleum products are given in the 1946 A.S.T.M. Standards both by colorimetry (A.S.T.M. D663-46T) (1) and by potentiometry (A.S.T.M. D664-46T) (2). In the colorimetric method the oil is added to a titration solvent consisting of denatured ethanol (10% methanol), the mixture is heated to boiling and is titrated while hot with aqueous KOH solution until a pink color with phenolphthalein is obtained. The potentiometric method follows the procedure devised by Lykken, Porter, Rullifson, and Tuemmler (3). The oil is added to an isopropanol-benzene titration solvent, and the effect of the addition of alcoholic KOH is followed by means of a glass electrode-calomel electrode system. The potentiometric method is recommended for dark or colored oils where the colorimetric endpoint is difficult to ascertain. It is stated in a note (1, 2) that acid numbers obtained by these two different methods may or may not be numerically the same. Lykken *et al.* (3) presented data referring to oxidized petroleum oils, indicating that no correspondence existed between acid numbers determined colorimetrically and potentiometrically.

Contrasted with these procedures, latest A.O.C.S. Official Methods give only a colorimetric method, A.O.C.S. Ca 5-40 (4), for the determination of acid numbers of vegetable and marine oils. This procedure resembles the colorimetric A.S.T.M. method

except that hot titration solvent is added to the oil rather than the alcohol-oil mixture heated. In the case of dark-colored oils the use of another indicator, Dr. Grubler's Aniline Blue, is suggested to replace phenolphthalein.

Colorimetric Determination of Acid Numbers

Neither of the existing official colorimetric methods is entirely satisfactory since many oils are not completely soluble in the denatured ethanol titration solvent, and heating the mixture may introduce errors. Titrations are not too reliable when carried out in a two-phase system formed with an insoluble oil. The indicator endpoint depends on the rate of shaking and on the time of shaking. Within the limited time for carrying out the titration, equilibrium conditions may not be established resulting in fading endpoints and poorly reproducible acid numbers. Heating the oil may cause sufficient modification to alter the acid number. This is particularly true in the case of oils which can be saponified; acid numbers which are too high result, accompanied by fading endpoints. Variation in the temperature causes changes in the amount of saponification and leads to poorly reproducible values. The hydrogen-ion activity varies inversely as the absolute temperature so that titrations carried out at different temperatures would yield different acid numbers. These variable factors may partially compensate each other, but this does not alter the conclusion that the experimental methods are not entirely satisfactory. Curve II in Fig. 1 illustrates the result obtained when a partially insoluble oil separates on cooling and the effect of reheating on the potentiometric titration curve. In curve III of Fig. 1 an example is given of the result of slow titration of a saponifiable oil.

Most of these difficulties may be traced to the choice of denatured ethanol as a titration solvent. Substitution of a solvent in which most oils were completely soluble should overcome many of these undesirable effects and should result in a more satisfactory method. An isopropanol-benzene mixture [as originally developed for the potentiometric method

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