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A New Industrial Process for Cottonseed[1]

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Described are the main principles of a new industrial process that permits the processing of cottonseed, producing a meal virtually free of free gossypol and of bound gossypol both and considerably improving the oil-refining yields.

A descriptive summary is given of the plant required and of the work cycle followed in the industrial establishment already in production for many years in Italy.

IN THE LAST 20 years two problems have received special attention in the field of cottonseed processing technology. The first was to eliminate the toxicity of cottonseed meal and the second was to improve the refining yields of the crude oil obtained by the crushing of cottonseed.

Regarding the first problem, it is known that the major source of the difficulties encountered in the use of cottonseed meal as a feed-stuff lies in the presence of a toxic pigment called gossypol. Almost all commercial meals and cakes contain only a small amount of free gossypol because, before crushing, the ground seed is subjected to a prolonged treatment with directly applied steam, which inactivates the gossypol insofar as it favors the combination of this product with the seed protein.

By this means the "cooking" of the seed solves to a partial extent the problem of the employment of cottonseed meal but at the cost of the nutritional value because the protein-gossypol compounds formed cannot be assimilated. Therefore important parts of the proteins present are not available. It has, in fact, been shown that the more prolonged and drastic the cooking, the less the nutritional value of the meal (1).

It is clear that the ideal solution would be to eliminate completely all the gossypol present in the seed, prior to cooking, so as to eliminate not only the "free" gossypol content but also the gossypol "bound" to the proteins. In a study made in collaboration by the Texas Agricultural Experiment Station and other institutes of the United States the conclusion was reached that "this would suggest that, if a suitable manufacturing method can be developed to produce meals containing only small amounts of both total and free gossypol, these would probably be meals of exceptionally high nutritional value, provided that the solubility of the protein remained high" (2).

In theory the total elimination of the gossypol is possible by the use of a solvent, such as butanone or acetone. Research has yielded satisfactory results. Meal directly purified of gossypol by extraction by solvents (butanone) have shown a nutritional value higher than that of soya meal (3,4). However the employment of such solvents has not been adopted in practice because they extract not only the gossypol but also the oil, which would be so impure as to be, in practice, unrefinable by ordinary means.

Another system, proposed recently by the Experimental Engineering Station of Texas, consists in the employment of n-octylamine, which would dissolve the gossypol. This method however is still being studied.

The second problem of major importance in the technology of the processing of cottonseed is that of refining loss and oil color. Because of the impurities contained in such oil (gossypol, phosphatides, etc.) ordinary methods of refining result in high refining losses.

Therefore, in the case of oils of medium acidity, the full loss of oil reaches values treble or more the acidity of the initial oil. More accurately to value these losses, reference must be made either to the "Wesson Loss" or, better still, to the "chromatographic loss," showing in the case of each oil the amount of the fatty acids and impurities. The loss factor is expressed by the ratio of the loss, practically checked in the refining process, to the chromatographic loss. For the batch-refining kettle process this loss factor rises between values of 2 and 2.5 for it is affected both by the acidity of the oil and its content of impurities.

Such high values, tolerable only with oil of low acidity and high purity, become serious whenever very acid oils from badly stored seeds must be processed. If such is the case, the real loss of oil in the refining process may reach 10% or even more of the oil treated.

Various ways of reducing these losses were studied. The simplest consists of centrifuging the soap stock to recover part of its neutral oil content. A better result is obtained by using two refining stages. First, slightly more than the theoretical amount of caustic soda suitable for the oil acidity is used. Thus complete neutralization results, with the oil unbleached. Then the whole mass is centrifuged to recover the most oil-impoverished soap stock, and the dark neutral oil is given a second treatment with caustic soda to attack the remaining gossypol and other impurities. This is followed by a second centrifuging, from which a neutral oil of good color results.

Later some continuous processes were studied in which the refining was carried out continuously with an exactly-measured amount of caustic soda. These plants normally use centrifugals and proceed by a number of stages. The oil is degummed, then undergoes two successive neutralizations, and is finally washed. Each stage is followed by centrifuging. There are several types of this kind of plant. They are usually efficient, but they are very expensive, complicated, and suitable only for high output.

The "Vaccarino" Method

For more than four years at the G. & S. Vaccarino factory a new process has been employed for treating cottonseed. This removes almost completely the gossypol from the meal and at the same time solves the problem of oil neutralization with high yields (5,6,7).

This process, patented throughout the world in almost all countries (*U.S. 2,944,072,* 1960), is already in use on an industrial scale in a plant working 60 tons of cottonseed per day and marks a notable advance in industrial technology in this field.

The control of the new process is no more difficult than that of a hexane plant while the refining stage is simpler and the machinery required is far less costly than that required for continuous refining by existing types.

The cost of extraction is not much higher than for the usual extraction plants while the neutralization cost is of the same magnitude as that with up-to-date processes.

The color of the neutralized oil is lighter than that of the product of the kettle process, and moreover it needs only a subsequent bleaching with 0.2–0.5% earth.

The basis of the new process is to extract the cottonseed meal by means of a solvent, characterized by dissolving not only the oil but also the gossypol. Acetone is one solvent of this kind, and as its chemical-physical characteristics (*e.g.,* boiling-point, specific gravity, viscosity, etc.) are only slightly different from those of hexane, acetone can easily replace it by only moderate adaptation of a plant built for hexane extraction. A major difference between the two solvents is that, as acetone removes the water in the seeds, in the course of time it tends to hydrate itself. So that an acetone plant should have a rectifying tower to keep the acetone at the correct working concentration. The advantages of acetone over hexane are that its volatile fractions are more easily recovered and acetone-caused fires are easily put out by ordinary water jets. Moreover it should be noted that phosphatides and gums are insoluble in acetone, which is profitable because of oil neutralization losses.

Acetone extraction gives an exceedingly light-colored meal, which is virtually free from gossypol (less than 0.03% free gossypol and less than 0.5% total gossypol) and affords no comparison with any other type of commercially extracted meal. The oil content of the acetone-treated meal is normally 0.4–0.7%, that is, the same as in the product of the usual extraction plants.

The acetone miscella obtained by extraction is highly colored, which is readily understandable, considering that it contains all the dissolved gossypol. If this mixture be evaporated, as in extraction plants, a virtually unrefinable oil results.

The new process however achieves the oil refining while it is still in the acetone miscella. Water dilution follows the treatment with cold alkali. Thus not only is the separation of the free saponified fatty acids accomplished but also the separation of the gossypol, for gossypol produces an alkaline salt soluble in water.

Acetone miscella refining is easily accomplished without appreciable attack on the neutral oil. The resultant separation of the aqueous phase, containing soap and gossypol sodium salt, is neat. No emulsion is formed for the presence of the acetone prevents emulsion formation. During the last stage the use of a centrifugal separator, suitable for solvents, safely prevents any oil loss. The small quantities of insoluble impurities in the two phases remain in the centrifugal separator and are removed periodically.

The oil phase comprises a neutral oil, extremely clear in color and holding only 8–10% of acetone. Heat and live, superheated steam wholly remove the solvent, and a neutralized oil results.

The aqueous phase is heated to 110°C. thoroughly to remove the acetone, which is rectified and returned to the treatment cycle. A watery soap solution remains, containing the gossypol and other impurities. This solution can be used to recover the fatty acids by the normal acidulation process.

The employment of acetone in this process is based on the fact that this solvent combines the advantages of hydrocarbons and alcohol. In fact, in the first stage of refining, the acetone behaves like a hydrocarbon and permits the separation of the soapstock in the solid state, but in a form almost anhydrous and crystalline, completely unlike that obtained by employing a hydrocarbon. After the dilution phase the acetone behaves, on the contrary, like an alcohol, allowing the complete solution of soap, previously formed without emulsion formation, and the complete removal of the neutral oil in the upper layer. The neutral oil loss in the lower layer is negligible for the solubility of neutral oil in diluted acetone is virtually nil. And no appreciable traces of soap are found in the upper layer for the dry soap is soluble in water but not in concentrated acetone or in oil. In working conditions the upper layer is composed of a solution of oil and of acetone, virtually free of water.

Figures Showing Solubility Oil-Water-Acetone

These phenomena are readily understood from the study of the reciprocal solubility of the three constituents present.

As is known, neutral oil and fatty acids are soluble in all the proportions in pure acetone at suitable temperatures. Commercial acetone has normally an average concentration of 99.5% in weight ($d = 0.791$–0.793 at 20°C.), but in practice one has to reckon on a concentration of approximately 96% because the rectifying of recovered acetone by means of a column of normal height cannot exceed this figure.

Figure 1 shows the equilibrium of the water-acetone system, indicating the graphic calculation of a rectifying column fed with dilute acetone, containing the 75% by weight of water (48% mol). It shows that to have at the top of the column a distillation of 96.5% acetone by weight (90% mol), six theoretical plates should be used, which means about 10 practical plates. If packed towers are employed, this corresponds to approximately 6 m. of Raschig rings. Experience has shown that the height of these towers should be considerably increased, owing to the imperfect passage of the liquids and gases.

To have a precise idea of the phenomena occurring in the course of refining in acetone and the subsequent dilution, one must take into account the ternary diagrams of the acetone-oil-water system. Figure 2 gives the diagram relating to the mixture: bleached cotton-

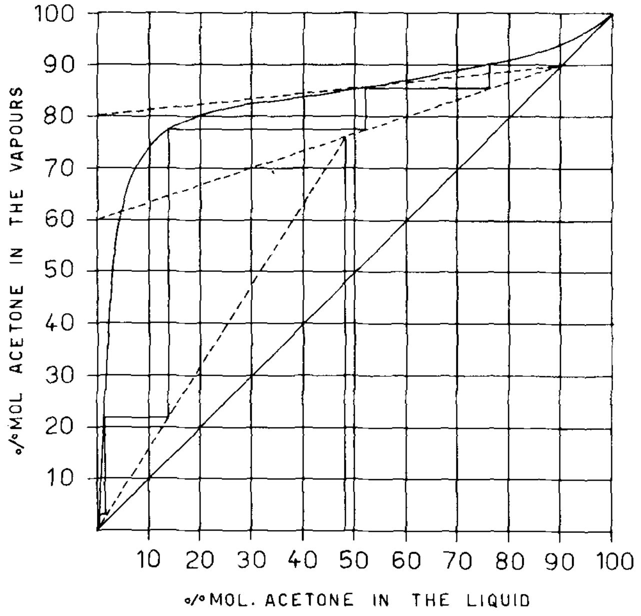

Fig. 1. Graphic calculation of an acetone rectifying column.

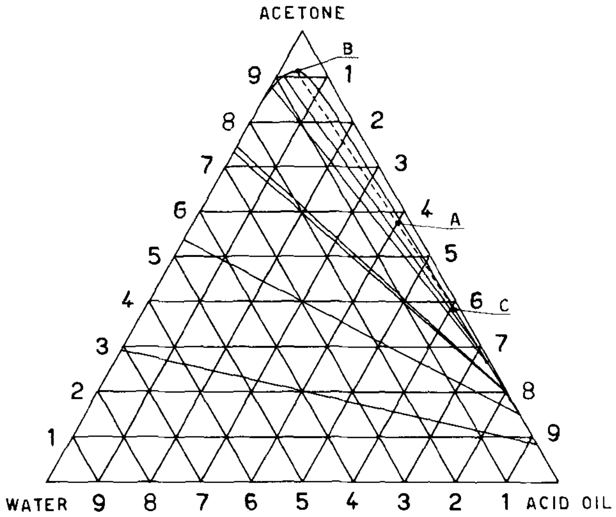

Fig. 2. Ternary diagram of the acetone-water-acid oil system.

seed oil of 5% FFA, pure acetone, and water at a temperature of 22°C.

An examination of this diagram shows that an homogeneous solution of the three components can occur only in the presence of very small quantities of water. The oil and acetone are mutually soluble in any proportion. However, in the presence of appreciable quantities of water, the mixture separates in two phases, one being composed almost entirely of oil with a small admixture of acetone and the other of acetone with varying amounts of water and oil. The quantity of oil in the latter depends on the quantity of water present, and it is easily shown that, for a ratio of acetone-water lower than 4, the quantity of oil contained in this is virtually nil.

The diagram in Figure 3 refers to the mixture of bleached, refined cottonseed oil, pure acetone, and water at a temperature of 45°C.

Comparing Figures 2 and 3, it is seen that, if the temperature is raised, the separation curves become slightly displaced for the solubility of oil in acetone (dilute) increases with the temperature.

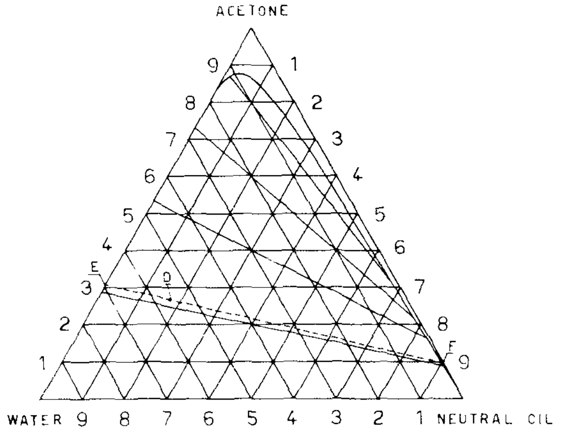

Fig. 3. Ternary diagram of the acetone-water-neutral oil system.

Let us follow the refining process based, for example, on a mixture initially composed of 1 kg. of oil of 5% FFA and of 1.5 kg. of 96% acetone, *viz.*:

Oil	1.00 kg. = 40.0%
Acetone	1.44 kg. = 57.6%
Water	0.06 kg. = 2.4%

We see that this composition in Figure 2 gives the point A, situated in the nonhomogeneous zone of the solution. The composition of the two phases present is determined by tracing the "tie-line" through A and marking the intersection with the solubility curve. Thus points B and C are obtained, corresponding to the compositions:

B) 90.5% acetone	C) 38% acetone
4.5% oil	61% oil
5.0% water	1% water

If the refining is done with 45 g. of 50% caustic soda, corresponding to a little more than triple the amount required to neutralize the free acid and if dilution with 3 kg. of water follows, then there is a final total of:

Neutral oil	0.950 kg.
Acetone	1.440 kg.
Water	3.080 kg.
Soap and excess anhydrous soda	0.075 kg.

If the soap and caustic soda are omitted, the mixture has the following composition:

Neutral oil	17.3%
Acetone	26.3%
Water	56.4%

This composition on the ternary diagram of Figure 3 (referring to the neutral oil-acetone-water mixture at 45°C.) corresponds to the point D. Tracing the tie-line from this point, the points E and F are obtained, which correspond, respectively, to the compositions:

E) 0 % neutral oil	F) 90.5% neutral oil
30.5% acetone	9.2% acetone
69.5% water	0.3% water

Thus, after dilution with water, theoretically no trace of neutral oil remains in the lower layer while in the upper layer, since the traces of soap may be considered nonexistent, the quantity of water present is negligible.

It may be deduced that a refining process, as described, produces yields unobtainable by other methods. On the one hand, the excess alkali does not at-

FIG. 4. Acetone continuous refining section (general view).

tack the neutral oil, and, on the other, there are no losses because of mechanical entrainment. The centrifuge is operated in the most positive fashion to prevent loss since the soap does not appear as a compact paste but as a perfectly limpid solution.

In this way, by pressing oils of average acidity, the refining losses are exceedingly low. For filtered oils, with few impurities, the loss factor is of the order 1.4 to 1.8, and the chromatographic loss is of the order 1.2 to 1.6. In oils containing many impurities the total loss would obviously be greater, but the neutral oil loss, in absolute value, remains virtually unchanged.

The neutral oil obtained by this process has a red Lovibond color, measured by the Lumetron colorimeter of 8 to 12, even in oils of high acidity coming from partially-impaired seed. When it is bleached with 0.5% of earth, it gives an oil of 2 to 3 red Lovibond. This value can be lowered by increasing the amount of bleaching earth.

The Industrial Process

The above process has been applied industrially for more than four years at the factory G. & S. Vaccarino. The plant consists of a crushing section, an extraction section, and a continuous refining section, operating in acetone. The crushing section is completely traditional: it comprises a Carver-Murray seed delinting and hulling plant and a battery of Olier continuous presses. These last do a precrushing work, leaving 18–20% oil in the cake. Since a grade of crushing is modest, no excessive conditioning of the meal is needed before pressing; a heating of 15 min. is sufficient.

The extraction section comprises two rotary type of extractors by Olier of 12,000 liters each, working in the usual way, with the difference that acetone is used instead of hexane.

Any other type of plant could be employed however without significant modification, apart from the elimination eventually of the plant for the recovery of uncondensed gases with active carbon. These should preferably be replaced by a contact condenser operating with water or with oil. The mixture obtained from extraction must be partly concentrated to obtain the ratio of oil to acetone of 1:1.5, which is best for the subsequent refining process.

The continuous refining section shown in Figures 4 and 5 is illustrated schematically in Figure 6. It should be noted that this can work not only the oil-acetone mixture obtained from the acetone-extraction plant but also the oil obtained in the pressing section or hexane-extracted oil of other sources. To do this, one has only to add such oils to the concentrated miscella obtained from the acetone plant. Of course, it is necessary to regulate the concentration so that the ratio of the total oil present to acetone is always that which is recommended.

The oil-acetone miscella from the extraction plant and the pressed oil are transferred from the tanks a and b by means of pumps P_1 and P_2 to the continuous refiner e. Flowmeters regulate the relative streams so that the ratio of oil to acetone remains constantly the prescribed 1:1.5. The continuous refiner consists of a horizontal mixer, to which is sent by means of pump P_3 the caustic soda coming from tank c in excess of the theoretical ratio required for neutralization. The neutralized miscella passes to the diluter f, similar in construction to the previous one, to which is sent, by means of pump P_4, the hot water coming from tank d to dissolve the soap formed. The neutralized and diluted mixture is introduced into the centrifugal separator g, which continuously separates the two phases. The oily phase is sent to the tank h while the aqueous phase, having passed through the heat-exchanger m, is sent to the rectifying column n. At the top of this column the rectified acetone is obtained by condensation in o and then collected in the acetone tank c,b, while at the bottom in the boiler is the acetone-free water, containing the dissolved soap and impurities present. This solution, which is at a temperature of approximately 100°C., is put into

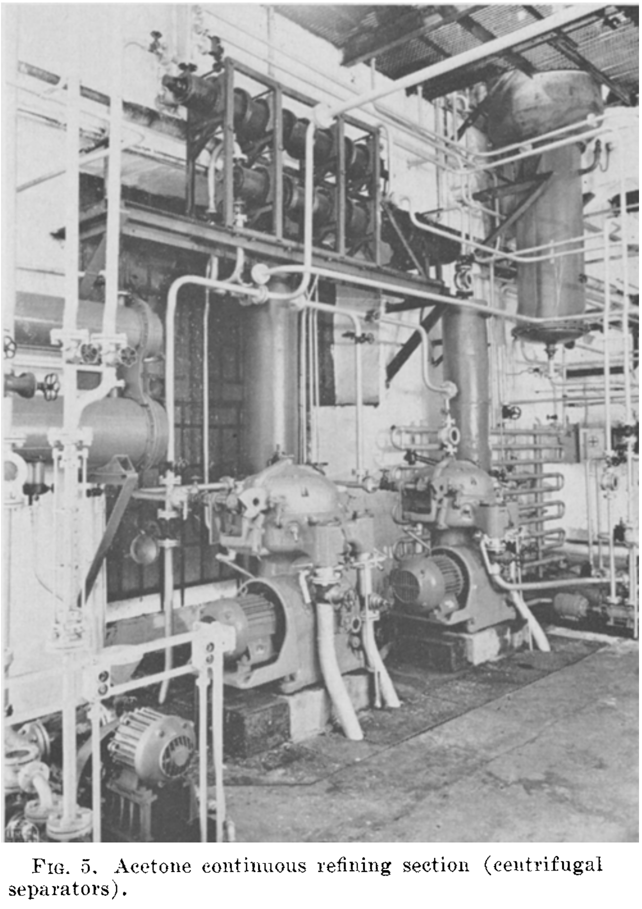

FIG. 5. Acetone continuous refining section (centrifugal separators).

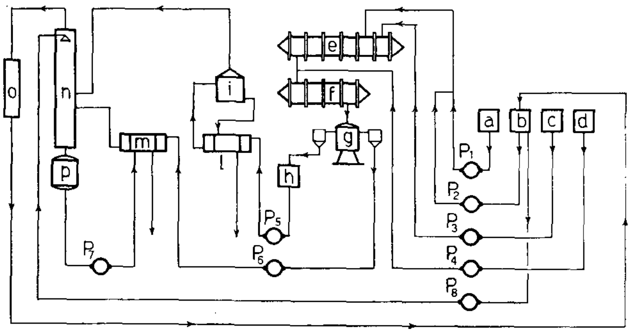

FIG. 6. Acetone continuous refining section (working diagram).

the heat-exchanger m to heat the solution to rectify. The cooled aqueous solution, on leaving m, can be used for the recovery of fatty acids by treatment with sulfuric acid.

The oily phase contained in the tank h is sent to the continuous distilling apparatus i, having passed through the heat-exchanger l. In i the acetone contained in the oily phase is completely separated while the refined oil thus obtained is cooled in the heat-exchanger l before being sent to the bleaching and deodorizing apparatus.

The acetone and water vapors obtained in i are also sent to the rectifying column n. The reflux of pure acetone required for this is withdrawn from the tank b by means of a pump P_8.

The very brief period of contact of oil and caustic soda during refining results in very low neutral oil losses; those by entrainment in the aqueous phase are negligible (0.1% at most of the aqueous phase). Since the average volume of the phase in question is 2.8 times the volume of the oil, the neutral oil losses by entrainment average 0.28% of the oil treated. Practically they can be made less since a share of the aqueous phase can be recycled to dilute the neutralized miscella. Thus only a portion of the aqueous phase is distilled, and a more concentrated final soap solution is obtained. This shows that the continuous process allows, in practice, the realization of a refining approaching theoretical.

It is useful to add that the regulation of the apparatus presents no difficulty because one works with wide margins of safety, and the handling of all the plant may be entrusted to a single workman of average qualifications.

Finally it must be stressed that the plant is not of high cost for all its parts are of extreme simplicity. The flowmeters are commercially obtainable, and the pumps are of current-production type. The centrifugal separator is of a type regularly made for other uses. A plant for neutralizing 30 tons of raw cottonseed oil costs in Italy about 40 million lires ($64,000).

The solvent losses are not much higher by employing acetone instead of hexane. The boiling point of pure acetone is 12–13°C. lower than that of hexane, which applies to the rectifying column, but in the neutralizing cycle acetone is diluted with water and this miscella boils at 75–76°C., that is to say, higher than the hexane boiling point. In Italy acetone costs 1.5 times hexane, and this ratio between the two solvents can be considered practical.

The cottonseed meal obtained by this plant has had a very favorable reception in the Italian and Central-European markets because of its rather light color and its proved efficiency as feeding for calves and milch cows. It is also used in mixtures for poultry and for young calves; its price, on a protein-content basis, is approximately equal that of soya meal. It must be remembered that this cottonseed meal, apart from being gossypol-free, contains a phosphorus content superior to that obtained by hexane extraction because the phosphatides (lecithin, etc.) are insoluble in acetone and therefore are not removed during extraction.

It may finally be remarked that if the production of gossypol-free cottonseed meal is not of interest, the acetone-refining system may be used only for improving the oil-refining yields. One may connect an acetone-refining section of the previously described type to a pressing plant (or hexane-extraction plant) of conventional type. This solution would be suitable for countries which have no special demands for quality in cattle food meals or in which it would be difficult to run an extraction plant (*e.g.*, in tropical countries). The employment of acetone, limited only to the requirements of the refining plant, cannot give rise to excessive difficulties. Moreover the cost of the plant and its relative operating costs are considerably reduced.

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Erratum

The authors wish to have Reference 6 in their paper, "Studies of the Chick Edema Factor. II. Isolation of a Toxic Substance," by Andrew Yartzoff, David Firestone, Daniel Banes, William Horwitz, Leo Friedman, and Stanley Nesheim (*38*, 60–62, 1961) deleted and the following substituted: "6. Ames, S.R., Swanson, W.J., Ludwig, M.I., and Brokaw, G.Y., J. Am. Oil Chemists' Soc., *37*, No. 4, 10 (1960)."