TABLE III

Effect of Changing Various Conditions on the Production of Cyclic Acids from Linseed Oil

Fatty material	Type of base	Excess base %	Solvent 3:1 ratio	Temperature, °C.	Time, hrs.	% Based on recovered crude acids[a]			
						Forerun	Monomeric acids[b]		Polymer[c]
							Cyclic acids	Straight-chain acids	
Refined linseed oil	KOH	25	Glycol	225	6½				
				295	6½	2.7	29.6	39.7	28.0
Refined linseed oil	KOH	5	Glycerine	250	4	1.7	15.0	59.8	23.5
Refined linseed oil	KOH	5	Diethylene glycol	220	14	......	27.5	45.0	27.5
Nonbreak linseed oil	KOH	10	Glycerine	235	13	......	10.0	40.0	50.0
Nonbreak linseed oil	NaOH	10	Glycerine	225	12	......	11.0	69.0	20.0
Nonbreak linseed oil	KOH	50	Glycol	225	10	......	30.5	52.0	17.5
Nonbreak linseed oil	NaOH	25	Glycol	295	1	2.7	32.4	38.1	26.8
93% Linolenic acid	KOH	50	Glycol	225	6	......	64.0	16.6	19.4
Tung oil	KOH	100	Glycol	210	6	......	56.2	17.8	25.0
Tung oil	None	......	Glycol	210	11	......	6.0	49.0	45.0

[a] The percentages of forerun, monomeric, and polymeric acids were determined by vacuum distillation of the recovered crude acids.
[b] The percentages of cyclic and straight-chain acids were determined by hydrogenation of the monomeric acids and removal of the saturated straight-chain acids by low-temperature crystallization from acetone.
[c] In all cases the polymer is at least in part a polyester.

Diethylene glycol is a convenient solvent if the cyclization is run at atmospheric pressure since its reflux temperature is somewhat higher than that of glycol.

Glycol can be used at temperatures up to 295°C. (Table III), provided that pressure vessels are adequate. At 225°C. the reaction mixture produces a pressure of about 30 to 40 p.s.i.g. whereas at 295°C. the pressure is about 250 p.s.i.g., and it increases slowly but constantly as cyclization continues. This increase may be caused by slight decomposition of the linseed oil, as indicated by the presence of a low-boiling forerun or else by decomposition of the glycol itself.

Alkali is apparently a catalyst for the cyclization, also for the conjugation of the triene system, as indicated by the results with tung oil (Table III). The ultraviolet and infrared spectra, as well as the physical constants of the cyclic acids obtained from tung oil, agree very well with those found for the same materials derived from linseed oil. The best conversion reported for eleostearic acid to a cyclic product by a purely thermal means was about 25% (4) whereas alkali treatment of tung oil (about 80% eleostearic) resulted in about a 70% conversion based on the eleostearic acid present.

As previously stated, evidence indicates that cyclization of the conjugated system occurs with the formation of vicinal-disubstituted cyclohexadienes as the principal products. This material differs from the product prepared by MacDonald (3) by heat treatment of linseed oil in that our material exhibits pronounced absorption above 255 mμ in the ultraviolet characteristic of cyclohexadiene while MacDonald's product does not.

Evidently the reaction proceeds by a base-catalyzed ionic mechanism of some sort. Further speculation on the mechanism of formation of the varied products seems futile until a more detailed study of their structure is undertaken.

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Plant-Scale Operations for Degumming, Caustic-Refining, and Water-Washing Soybean Oil by a Two-Step Continuous Process[1]

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Operation of a four-tank-car-per-day plant, using a Duozon[3] and a Hydrazon[3] "in series" to perform continuous degumming, caustic refining, and water washing of soybean oil is described. A simplified flow sheet, illustrating the process, and a detailed functional description of the degummer and the caustic refiner-water washer are given. Typical plant-operating data for this versatile, low-cost plant are presented.

PODBIELNIAK INC. entered the vegetable oil refining field in 1955. During the ensuing years a number of technical papers have been published in the Journal of the American Oil Chemists' Society. Continuous water-degumming of soybean oil on a commercial scale by means of a centrifugal type of oil-gum separator, operating under pressure, was reported in 1956 (1). The use of a multistage, countercurrent centrifugal contactor, for efficient removal of dis-

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solved soap from caustic-refined oil was also described (2). Recently the development of a unique centrifugal machine which combined the design features of the oil-gum separator and the multistage contactor was announced (3). This permits separation of the oil-soap phases and simultaneously, countercurrently water-washes the oil.

The present paper will describe the operation of a 4-T.C./day plant, employing a Duozon (degummer) and a Hydrazon (caustic refining-water washer) "in series" to degum, caustic-refine, and water-wash extracted soybean oil.

History

Degumming of extracted soybean oil at the Iowa Soya Company was first begun on a plant-scale basis in the spring of 1957. Consideration was given to both the open and hermetic type of centrifuge units; however because adequate space and operating personnel were available in the extraction building, pressure-tight, sealed equipment was favored. The machine chosen was a stainless steel Duozon with 3 seals and a capacity of 10,000 lbs. of crude oil per hour.

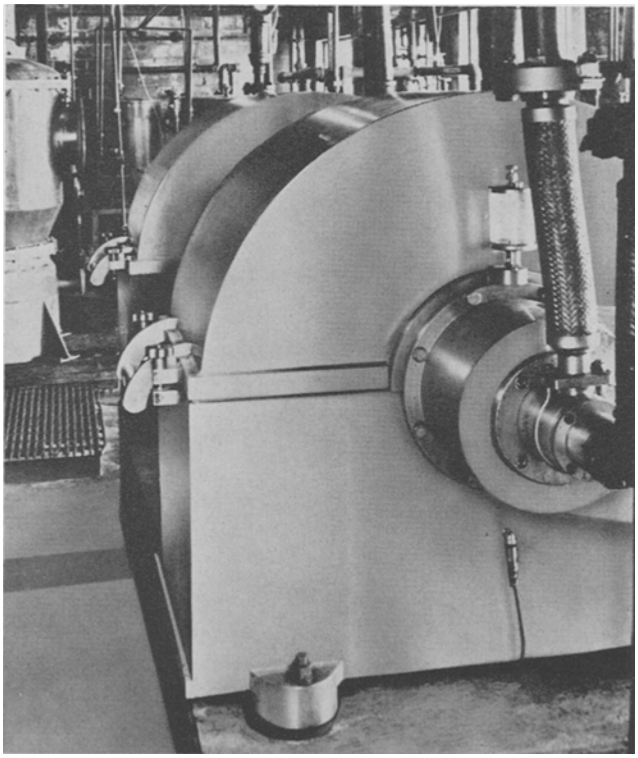

Fig. 1. Duozon (foreground) and hydrazon (background) installed at Iowa Soya Company, Redfield, Ia.

A typical gum produced by this plant would be of the 67–68 A.I. (dry basis) and contain approximately 35% moisture. This machine has been operated continuously at different periods at 10% over its rated capacity without a drop-off in performance.

In 1958 the Iowa Soya Company decided that they could produce a once-refined oil as they had adequate physical space available adjacent to the degumming equipment and the present operating personnel could be used.

A stainless steel Hydrazon, 4-seal machine, was selected for this operation. An experimental unit was placed in service during the summer of 1958, from which valuable design data were obtained for the construction of the present production unit.

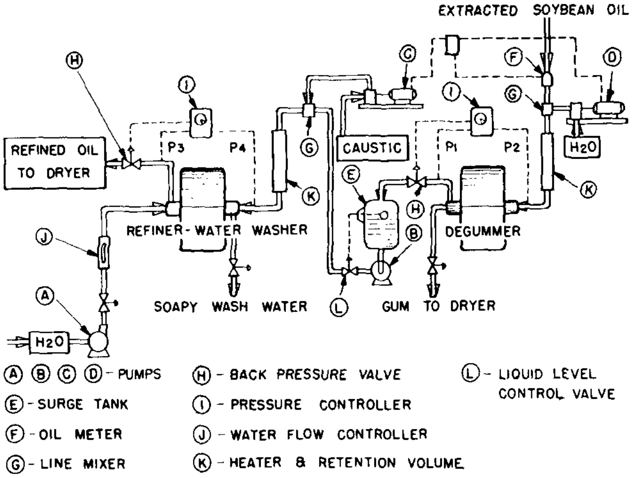

Fig. 2. Continuous 2-step process for degumming caustic refining and water-washing soybean oil.

Figure 1 shows the two machines installed in a floor space about 12 x 24 ft. on the mezzanine of the extraction building. All accessory equipment for operation of the Duozon and the Hydrazon, including automatic control panel, are installed in close proximity to the machines.

During the first months of operation considerable experimenting with wash-water temperature, caustic strength, and amount of excess caustic was conducted by Iowa Soya chemists and engineers. Necessary modifications to the machine were performed by Podbielniak, and the cooperative effort of these two companies resulted in the present satisfactorily-operating plant.

Present Operations at Iowa Soya

Stripped soybean oil from the extraction operations is sent to the refining plant to be either degummed and vacuum-dried or degummed, caustic-refined, water-washed, and vacuum-dried, depending on the sales requirements.

The 2-step process for continuous degumming, caustic refining, and water washing of the oil is best illustrated by the flow sheet, Figure 2. Oil is pumped through an oil meter which sends a low-voltage direct-current impulse to an electronic amplifier, which in turn controls the degumming water rate in direct proportion to the oil flow. Water enters the oil stream through a line mixer, and subsequently the mixed oil

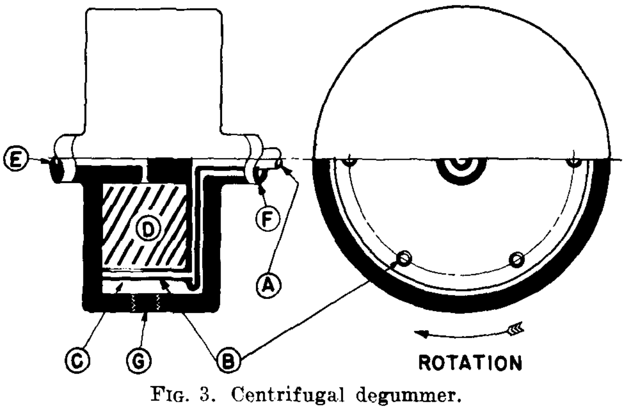

Fig. 3. Centrifugal degummer.

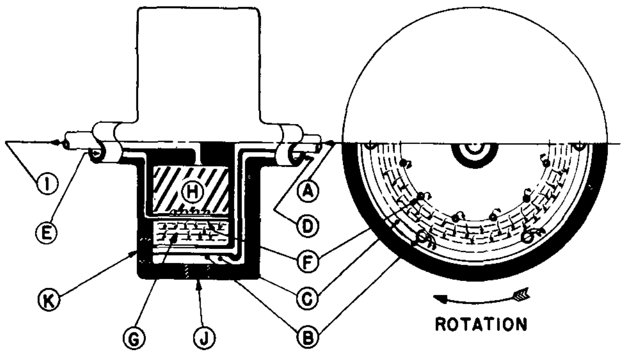

FIG. 4. Centrifugal refiner-water washer.

and water flow through a 6-min. retention volume tank, thence to the Duozon.

The Duozon separates gum from the oil and sends it on to the gum drier. Degummed oil flows from the machine through a back pressure-control valve into a small-volume, vented surge tank. This tank is equipped with a Leveltrol, which automatically controls the rate at which oil is pumped to the second step, maintaining a constant level in the tank, thus regulating "out-flow" exactly equal to "in-flow."

A second reagent pump, also controlled from an oil meter, injects caustic into a line mixer, where reaction of caustic with free fatty acids and phosphatidic materials takes place. The mixture of oil and soap thus formed flows through a volume-retention tank on to the Hydrazon.

Deionized wash water is pumped and metered countercurrently through the Hydrazon to wash soap from the oil. This wash water joins the soap layer and leaves as a soapy wash water.

Oil from the Hydrazon then flows through a back pressure-control valve on to the vacuum drier. The soapy wash water in this plant is discarded to the drain; however it is entirely feasible to recover fatty acids by means of acidulation, employing a simple line mixer and providing facilities for collection of the acids. Further studies are being made to determine the economics of reclaiming fatty acids from operations, where the refining loss is already quite low.

On both the degummer and caustic refiner-water washer, pressure taps are installed in feed and discharge oil-pipe lines. These are connected to differential pressure transmitters, which in turn send low-pressure air signals to differential pressure controllers.

Principle of Operation

The machines used in this process are illustrated in Figures 3 and 4. These are horizontally-mounted rotating drums or rotors with mechanical seals at each end of the shaft for feeding and withdrawing liquids. The Duozon is the same as used commercially for some five years. However the Hydrazon differs considerably from the modified Podbielniak Contactor described by Mattikow (4). The differences are principally in the internal-design details of liquid-entering velocities and the orientation of feed weirs in an area where the behavior of process liquids under centrifugal force has heretofore been unpredictable. The principle of operation for both Duozon and Hydrazon is described as follows.

TABLE I

Typical Operating Conditions

First step	
Rotor speed	2100 r.p.m.
Oil feed temperature	175°F.
Inlet pressure "mix"	90 p.s.i.g.
Discharge pressure, oil	60 p.s.i.g.
Operating pressure differential	30 p.s.i.g.
Water treat to oil (weight basis)	2.5–3.0%
Second Step	
Rotor speed	2100 r.p.m.
Oil feed temperature	160–170°F.
Inlet pressure "mix"	89–90 p.s.i.g.
Discharge pressure, oil	62–65 p.s.i.g.
Operating pressure differential	25–26 p.s.i.g.
Temperature wash water	200°F.
Caustic treat 20° Bé (weight basis)	1.0–1.3%
Wash water (weight basis)	15–17%

Figure 3 illustrates the Duozon. Oil mixed with gum enters at (A), flows radially through conduits and laterally through the weir type of distributors (B), and escapes at low velocity into the rotor. Because of the difference in density between the oil and the gum, centrifugal force causes the heavier phase (gum) to move outward into the annular space (C), where it forms a layer of uniform thickness. The oil separating from the gum moves toward the center of the rotor through specially-designed clarifying elements (D) and leaves at the center of the shaft (E). A controlled back pressure applied to the degummed oil at (E) forces gum from the annulus (C) over a circular spill-over disc, causing it to return to the shaft and exit at (F).

TABLE II

Analyses of Oil

Crude extracted oil:	
Moisture content	0.20–0.30%
F.F.A	0.35–0.45%
Refined oil:	
Moisture	0.30–0.40%
F.F.A	0.2%
Soap (as NaOH)	20–25 p.p.m.
Phosphorus	8–15 p.p.m.
Refining losses [a] across second step	0.75%

[a] Losses determined both by analysis of soapy wash water and plant material balances.

Because of the relatively low G's (2,000) in the degummer it has been found that any meal or solids entering with the oil will stay suspended with the gum and continuously move out with it. Clean-out ports (G) facilitate cleaning when necessary. In plants producing "pure" lecithin, the oil must be filtered to remove any meal or other impurities prior to degumming.

In the Hydrazon (Figure 4) the oil-soap mixture enters at (A), moves similarly through distributors (B), and is turned loose in the rotor at relatively low velocities. The soap, being of higher density, moves outward into the annular space (C), where it is deposited with the least disturbance in a uniform layer. The oil separating from the soap flows toward the rotor shaft. However it must first flow through a washing section (G). Softened wash-water entering at (E) flows into specially designed distributors (F) and is released to wash the oil. The water flows outward, encountering oil which is flowing in the opposite direction, thus effecting true countercurrent, multistage washing of the oil. The weirs which distribute the water are purposely directed to the center of the rotor, thus causing the water to change its direction in a smooth arc "trailing" the direction of rotation. This action causes the water to be fed gently into the oil in the form of a thin sheet or film at extremely low velocities to prevent emulsion.

Mixing of the water and oil for the best contact is accomplished by a series of concentric elements in the wash section, having fairly large orifices and spaced in such a manner as to obtain circumferential turbulence and redistribution of water. The oil emerging from the wash section enters a clarifying section (H) and finally leaves at (I). Water flowing away from the wash section joins the soap layer, dilutes it, and together moves over a circular spill-over disc, finally leaving at (D). A few pounds of back pressure, applied to the refined oil at (I), maintains a constant rate of flow of soapy wash water from the machine. In practice the differential pressure controller tied into the piping system keeps the machine ''in balance'' and operating continuously without loss of oil to the soapy water discharge.

These machines differ completely from conventional centrifuges because the ''mix'' is delivered to the rotor through specially-designed conduits and weirs, where at the point of entry or release of ''mix'' into the rotor the relative velocity is zero.

The gum picks up some energy as it continues its flow pattern; however slippage in viscous materials is negligible.

The washed oil however must give up energy as it flows back from its entry point and the concentric wash elements serve to slow down the oil. Turbulence created by slippage is sufficient to cause just enough gentle mixing of desoaped oil with water, avoiding serious emulsion difficulties in the wash-section area.

Typical Plant-Operating Conditions

Table I shows the pertinent operating data for the Duozon (Step 1) and Hydrazon (Step 2). It may be noted that the inlet pressure for the degumming operation is 90 p.s.i.g. and that the back pressure on the oil leaving is 60 p.s.i.g., or a differential of 30 p.s.i.g. In practice this differential may be varied from about 10 to 50 p.s.i.g. without materially affecting the operation of the machine. The gum leaves the machine at atmospheric pressure. The operating-pressure differential depends on the viscosity of gum and other process variables. Usually dry gums require the lower pressure differential.

For the Hydrazon the range of pressure differential may be wider because of the lower viscosity of the soap-wash water layer. The practice at Iowa Soya however is to set the pressure differential about the same on both machines.

Here again these units differ from centrifuges *per se* because they do not contain so-called ''ring dams,'' and the operator may change the main interface in the rotor by simply resetting the pressure differential at the control panel.

Analyses of the crude and refined oils are shown in Table II. The oil from the vacuum drier is HCl break-free and compares in quality with similar oils refined by more complicated, 4-step, mixer-centrifuge practice.

The low refining loss of less than 0.75% across the refining-water washing step is attributed to the efficiency of the first step. The amount of neutral oil in the soapy wash water is very low.

Versatility an Important Advantage

Iowa Soya Company has found the Hydrazon to be quite versatile in this process application. It can be used effectively either as a second-step machine or as a basic degummer. As a degumming unit it exceeds the rated capacity by 100% while for caustic refining-water washing it has achieved 10% over rated capacity without drop-off in performance.

The Hydrazon can be changed from a second-step machine to a degummer in a matter of minutes and can be changed back again to a second-step operation by a simple exchange of feed nozzles.

This is important in achieving maximum flexibility for a given plant installation where the sales demand varies from degummed oil to refined oil.

The versatility afforded by the Hydrazon permits the plant to be operated with two machines ''in parallel'' for degumming or ''in series'' for degumming, caustic refining, and water washing. The change-over requires only the changing of valves and the lining out of the process piping.

Labor Saving

The Duozon and Hydrazon do not require disassembly for cleaning and washing and actually may be operated weeks on end without interruption to production.

Cleaning of the degummer merely requires displacement of the gum by decreasing the pressure differential until all of it is pushed out of the rotor, followed by oil displacement (using hot water), then flushing with hot water after the rotor has been stopped and rotor clean-out plugs have been removed.

Similarly the second-step machine is cleaned by shutting off the oil, displacing the rotor contents with water, and flushing hot water through the clean-out ports after the rotor has stopped and plugs have been removed.

Conclusions

In conclusion, Iowa Soya Company has operated a 2-step continuous process for degumming, caustic refining, and water washing of soybean oil over a period of several months, during which they concluded that the equipment produces a quality-finished product with the minimum amount of labor cost and with refining losses across the second step of less than 0.75%.

Acknowledgment

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