

FIG. 4. Top panel—sand trails of an isobutyl-(3)-conjugated-soy-(1) copolymer baked at 150°C. without drier. Bottom panel—sand trails of a nonconjugated linseed vinyl ether homopolymer baked at 100°C. without drier.

TABLE III

Effect of Iron Naphthenate on Drying Time of Films at 180°C.^a

	Tack-free time	Dry-to-touch time
	min.	min.
With drier ^b on Al.....	45	8
No drier on Al.....	>120	25
With drier ^b on Fe.....	45	8
No drier on Fe.....	75	15

^a Isobutyl-(3)-conjugated soy-(1)-vinyl ether copolymer.

^b 0.1% Fe as naphthenate.

containing drier; the catalytic effect of the black iron disc is masked by the presence of iron naphthenate.

A comparison of the relative effectiveness of cobalt and iron naphthenate on drying time may be made

from an inspection of the data in Tables I, II, and III. The conclusion that iron naphthenate contributes to faster drying is in agreement with other observations made (5).

Summary

An apparatus has been described for determining the drying time of protective coatings at elevated temperatures, and tests have been made with vinyl ether formulations. The device is essentially a miniature Sanderson drying-time meter constructed in an oven where temperatures up to 260°C. can be maintained. Tolerances were made on the order of 0.015 in. for gear clearances and bearing expansion. A special high-temperature grease is the lubricant. Turntables, which make one revolution every 15 min., permit simultaneous evaluation of three films. Reproducible results have been obtained, and uniform conditions apparently prevail throughout the oven.

Coatings are prepared by the spinning disc method, and under controlled conditions the film thickness is approximately 0.15 mil. "Tack-free time" and "dry-to-touch time" are determined by the usual method of removing sand from the disc. Discs were stamped from aluminum as well as black iron, and differences in drying times observed. Coatings on black iron dry faster than those on aluminum, and it is presumed that iron plays the role of an oxidation or polymerization catalyst.

Acknowledgments

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A New Concept in Vegetable Oil Refining Automation

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THE REFINING of vegetable oils began as an art with the kettle or batch process. Continuous refining has been made possible by the use of proportioning control for addition of reagent to crude oil, temperature control, and centrifuges for more rapid separation of oil from gum or soap stock. Plants of large refining capacity which use multiple centrifuge installations do not lend themselves however to practical automation. The lack of automation requires the attention of a skilled operator.

This paper presents our approach to automatic continuous vegetable oil refining by using unique process equipment, the design of which is suitable for automatic control. Essentially the process consists of two centrifugal contactors: a) a phase separator, re-

ferred to as Duozone, which separates refined oil from gum or soap stock; b) an extractor known as Hydrazone designed for water extraction of dissolved soap from the primary refined oil.

These machines have been described in a recent paper (1). The Duozone combines a large coalescing surface and high retention time with centrifugal force. The gravities however are not excessive enough to cause meal to hang up in the rotor; rather it is discharged continuously with gum or soap stock. Because of pressure operation and the high through-put capacity, a single unit may be used for primary gum or soap stock operation in refineries of two to 10 tank cars per day capacity. Gum or soap discharges from a single pipeline.

Similarly a single unit is used for multistage water-

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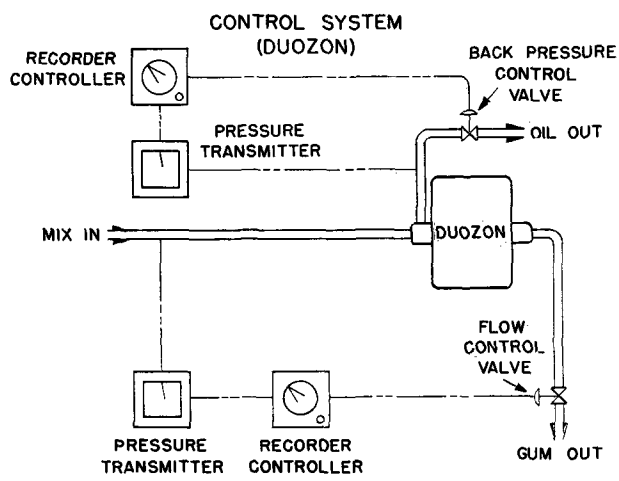


FIG. 1.

washing operation. Four or more countercurrent stages result in practically complete removal of impurities with less than one-fourth the amount of water required for the batch process.

The control system (Figure 1) applied to the single Duozone consists of pressure transmitters, automatic recording controllers, a back pressure-control valve in the oil discharge, and a flow-control valve in the gum discharge. The back pressure-control valve in this instance serves the purpose of a readily adjustable ring dam and is the primary control element. During start-up a gum or soap stock seal is formed while the gum discharge valve is closed. In operation this valve closes in the event of upset, precluding loss of oil. The mix inlet pressure serves as the primary measure for control of the gum discharge valve. Operation is achieved by simply setting the control to open the gum discharge valve when the mix inlet pressure reaches 90 p.s.i.g. Normally the back pressure-control valve is set at 70 p.s.i.g. or a differential of 20 p.s.i.g. This control system assures automatic operation under all conditions.

Other basic control functions associated with continuous refining include those for temperature, flow, pressure, and liquid level. A review of these systems follows.

Figure 2 illustrates the components of a control system for heating oil. Measurement of temperature is achieved by a primary sensing element working in

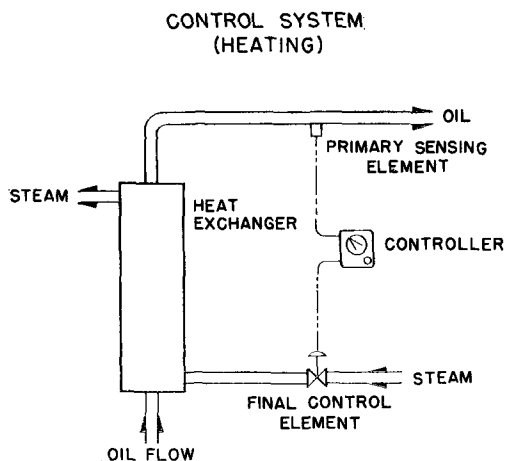


FIG. 2.

conjunction with an automatic controller to maintain the system in balance with a temperature set-point. The control valve is pneumatically linked with the controller to regulate the steam flow.

WE have used two methods of flow control. The first (Figure 3) employs a variable area flowmeter as a primary measuring element, which converts the flow variable into a pneumatically transmitted signal relayed to the automatic flow controller. The controller maintains the desired flow rate by operating a pneumatic flow control valve. Another method used (Figure 4) incorporates an orifice plate principle with a kinetic manometer sensing the differential pressure and converting this to a pneumatic signal relayed to the controller.

CONTROL SYSTEM (LIQUID FLOW—FLOWMETER)

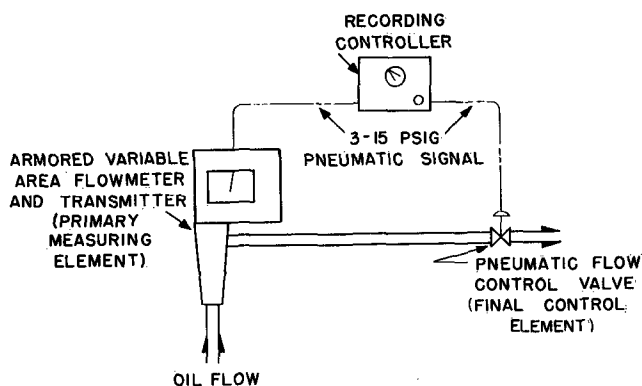


FIG. 3.

CONTROL SYSTEM (LIQUID FLOW—D/P CELL)

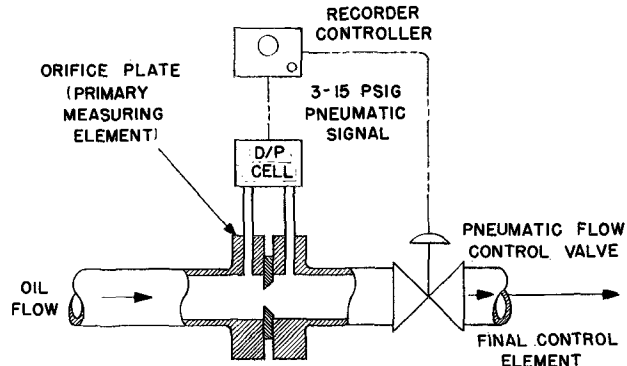


FIG. 4.

Because of the liquid characteristics encountered, a filled pressure transmitting system (Figure 5) is used. The main pressure sensing element is interlinked with the automatic control which maintains the desired pressure by operating the pressure-control valve.

The liquid level control system (Figure 6) which we have used successfully consists of a differential pressure-sensing device which converts corresponding liquid level to a pneumatic signal working in conjunction with a controller and pneumatic valve. This control system is used to tie together the operation of the Duozone and Hydrazon to provide a continuous process, utilizing the basic controls described.

Figure 7 is a typical flowsheet of a vegetable oil

CONTROL SYSTEM
(PRESSURE)

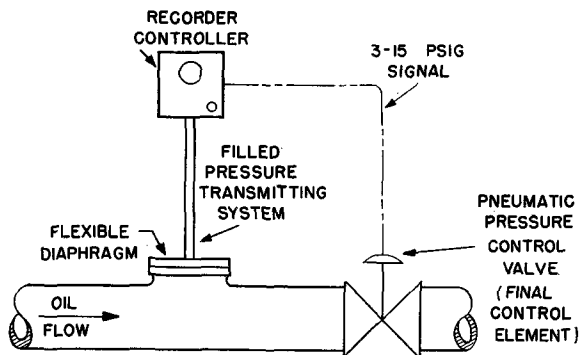


FIG. 5.

CONTROL SYSTEM
(LIQUID LEVEL)

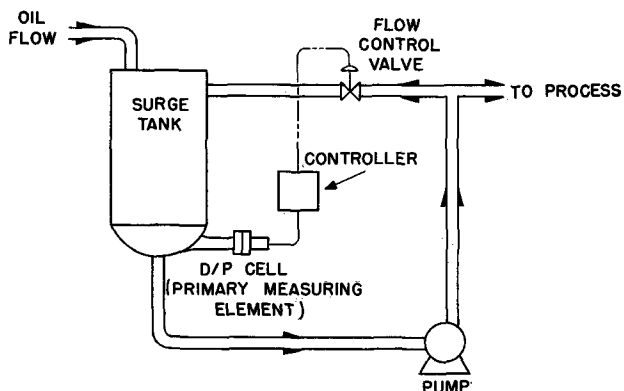


FIG. 6.

refining installation for degumming and water washing, using the Staley 50 Oil Process, or caustic refining if desired. Addition of the reagents, including acetic anhydride, degumming water, and hydrogen peroxide, to the controlled flow crude oil is accomplished by means of automatic-cascade ratio controls. The wash water required for the extraction step is also ratio-controlled from the crude oil flow. Any change in oil flow rate will immediately effect a correcting change in the flow rates of all other process liquids. The temperature of the oil mixture is con-

CONTROL SYSTEM
(50 OIL PROCESS)

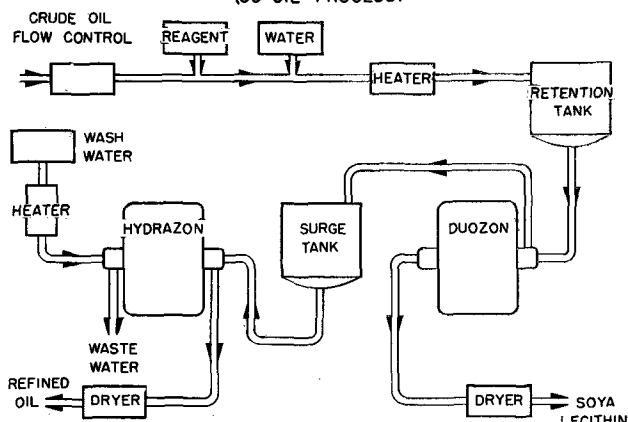


FIG. 7.

trolled in the heat exchanger prior to its entry into a level-controlled retention tank. From the retention tank it is pumped into the Duozone. The gum discharged from the Duozone passes through a temperature and pressure-controlled vacuum drier. The vacuum is continuously recorded on a remote control panel instrument. Dried gums are processed into soya lecithin.

Refined oil from the Duozone flows into a level-controlled surge tank and is then pumped to the Hydrazone, countercurrent to wash water. This surge tank serves as the main interconnection between the two machines. Refined oil, after washing, flows into the oil vacuum drier, which incorporates an automatic liquid-level control to insure continuous discharge.

Although designed primarily for degumming and water washing, the plant process control flowsheet and associated equipment lend themselves to versatile and flexible operations for oil refining. For example, the installation may be used for processes such as caustic, ammonia, and soda ash refining.

FOR the ammonia refining process which must operate under pressure, we have found the Clayton Proportioning Pump and associated controls to be especially suitable and most satisfactory for adding the reagent. This system consists of a specially designed piston type of metering pump with variable-speed driving mechanism, a meter generator, and an electronic amplifier-controller.

The pump is adjustable to length of stroke and number of strokes in linear function according to the main flow of oil through the meter generator. A valve seat sleeve material in the pump absorbs fluid and becomes tight-fitting, thus obviating slippage. It is also noncorrosive and self-lubricated. The cylinder length is adjustable according to the required capacity, thus always wiping out clean contents at each

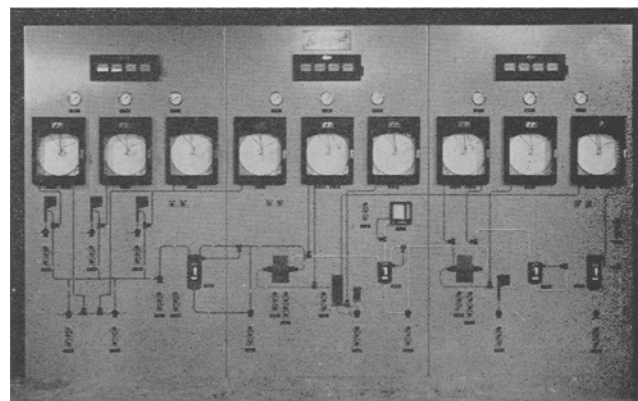


FIG. 8. Control panel used in a refining installation.

stroke regardless of how short or long. Precise measurement and addition of reagent to the oil regardless of its flow and pressure of the system are essential to the continuous process.

A graphic type of control panel used in a refining installation is shown in Figure 8. This panel incorporates all ratio recording controls as well as the liquid level, pressure, temperature, and vacuum-recording controllers. The graphic flow diagram includes pump motor, start-stop stations with associated pilot lights, liquid-level indicators, and alarms. Flashing alarm annunciators located at the top of the panel serve to indicate upset conditions.

Automatizing the separation of gum or soap stock from vegetable oil is an innovation which, when combined with the basic control methods described, satisfies all the requirements of precise and vigilant operation of a continuous process. Plants have operated 24 hours per day, seven days a week, for periods of six months and longer without interruption.

In conclusion, we emphasize the advantages of this automatic control system. Increased production and quality control are attributed to elimination of the human element. Centralized control and graphic presentation simplify supervision of plant operation. The flashing alarm system pinpoints trouble locations immediately, preventing oil loss otherwise unnoticed.

Automation of this type eliminates the necessity for operators skilled in the art of vegetable oil refining. They need only to be given the analysis of the feed stock; then they can set the controls and press the buttons.

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n-Deca-2,4-Dienal, Its Origin from Linoleate and Flavor Significance in Fats^{1, 2}

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A SERIES of methyl ketones, characterized as their 2,4-dinitrophenylhydrazones,⁴ recently was identified in the deodorization distillate of fresh milk fat at this laboratory (12). This series was composed of the straight-chain members containing odd numbers of carbons from C₃ through C₁₅. Whether other common fats and oils might yield the same group of ketones under similar conditions was considered worthy of investigation. It was found difficult, if not impossible, to make the conditions for handling other fats the same as for milk fat. Distillates from cottonseed oil, soybean oil, beef tallow, and lard were evaluated. Since the preliminary processing of these fats was beyond our control, the negative findings obtained with respect to the series of ketones in their distillates are of questionable value. However the predominance of n-deca 2,4-dienal, as detected through its DNP-hydrazone, among the carbonyl compounds in distillates from all four fats was impressive and served as the stimulus for the investigations described below. Decadienal is "fantastically" potent as a flavor compound. Its flavor threshold value in water was determined to be 0.5 parts per billion. As will be shown, its formation through action of moisture and heat seems predictable from any fat which contains linoleate.

Experimental

Decadienal from Commercial Fats. Steam deodorization of fats and collection of distillates were performed for us through the kind services of R. J. Sims and associates of Swift and Company. The fats employed in the study were cottonseed oil, soybean oil, beef tallow, and lard, all in good condition and considered to be representative of the materials processed by industry. They were steam-deodorized in amounts of 3 liters each at 225°C. and 1 mm. Hg for 3 to 5 hr., using conventional laboratory deodorizing equipment

(12). The beef tallow, a fresh steam-rendered product, was deodorized at this laboratory. The thawed distillates from the four fats all had very pronounced odor reminiscent of fat used many times for frying. DNPhydrazones of carbonyl compounds in the distillates were prepared as follows. Each distillate, amounting to about 200-300 ml., was saturated with NaCl and then extracted four times with 50-ml. volumes of ethyl ether. To the combined ether extracts was added a DNPhydrazine solution prepared by dissolving 200 mg. of the solid reagent in 1 ml. of concentrated H₂SO₄, 2 ml. of H₂O, and 5 ml. of ethanol (abs). Extract and reagent were mixed with a stirrer for 1 hr., 25 ml. of H₂O were added, and the stirring was continued for an additional 15 min. The ether layer containing the hydrazones was evaporated under reduced pressure (water aspirator), and the residue was extracted by mechanical shaking for 1 hr. with 50 ml. of n-hexane. Hexane solutions derived from distillates of the four fats were employed as the source of samples for column and paper chromatographic separation of the DNPhydrazones. The column separation used Celite as support, nitromethane as immobile phase, and n-hexane as moving phase. This method was developed and brought to our attention by Bassette *et al.* (1) and is very similar to that of Monty (7). Use of the method in this investigation was precisely as described in reference 12. To follow separation of hydrazone bands on the chromatography column and to aid identification, the paper chromatographic method of Huelin (5) was employed. Although there was evidence of numerous hydrazones, in both paper and column separations, one red derivative (R_f 0.71, by the Huelin method, retention volume on a 50-g. [Celite] column 800 ± 20 ml. of hexane) predominated in intensity from all four fats.⁵

⁵ There were the following numbers of definitely observable hydrazone bands with mobilities greater than that of the acetone derivative: cottonseed oil—6, soybean oil—7, beef tallow—6, lard—9. Since hexane extraction seems to recover only DNPhydrazones of monofunctional carbonyl compounds with any degree of efficiency, the number of bands observed is considered only a partial accounting of the carbonyls in the distillate. At this point a decision was made to attempt identification of only the prominent red hydrazone and thus determine whether or not the same compound derived from all four fats.

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⁴ 2,4-Dinitrophenyl is hereinafter abbreviated DNP.