were not built into the instrument. With such good results obtained on the laboratory instrument, a 30-in. column was prepared and used on the process instrument. Figure 3 shows the still stream profile obtained with the column on the plant instrument during a Coco fatty acid distillation. The quantitative results compared favorably with those obtained by the chromatography of the same acids as esters.

This particular column packing shows great promise for the gas chromatography of unesterified fatty acids. The drawbacks of this column are that it requires higher temp than the polyester columns; the fatty acid emergence time is longer for a given column length; the unsaturated and saturated acids are not completely resolved. However, these disadvantages are more than offset by the fine symmetrical peaks and the excellent quantitative results obtained using peak areas alone. How long these columns will maintain their efficiency is not known at this time. The DEGA-

H_3PO_4 columns have operated as long as six months before replacement was necessary.

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Process Gas Chromatography of Fatty Acid Distillation Streams.[1] II. Design and Construction of the Process Chromatograph

E. H. STOLL, L. D. METCALFE, N. E. NUDING, G. P. HARTSUCH and S. H. SHAPIRO, Research Laboratories, Armour Industrial Chemical Company, McCook, Illinois

Abstract

When applied to fatty acid process chromatography, conventional instrumentation is inadequate because of the temp required for effective vaporization of the sample. The instrument described uses a special injector operating at 300C for analysis of distillate streams containing fatty acids C_6 through C_{18}. Tape programmed operation presents analytical data as a chromatogram or as digital printout of electronically integrated peak areas. Details of construction are discussed together with some design problems.

Introduction

A TROUBLESOME, IF NOT a serious, problem hindering process chromatography of the fatty acids has been the necessity for converting these acids to their methyl esters before injection into the chromatograph instrument. By eliminating this step, the phosphoric acid column opened the way for designing a practical process analyzer which can accept samples of these acids directly from the process stream (1,2).

This analyzer was designed specifically to monitor continuously the composition of distillate streams in a fractionating process where the acids range from 6–18 atoms in carbon chain length. Because of the elevated temp needed in handling the higher boiling acids, special techniques and departures from conventional design were required, making the instrument somewhat unique. A description of its construction and operation are given here, and some problems encountered in its design are also treated. The chemistry

and column technology related to this project are covered in another paper (3).

Sample Handling

Since the materials in the processing stream require a temp of ca. 80C to keep them fluid, all pumps and sample lines leading into the chromatograph are steam traced. The hairpin column and its heater, together with the thermal conductivity detector, are housed in an insulated cabinet held at an environmental temp of 80C by a 750-w fin heater. The temp is regulated by a mercury bulb thermostat through its electronic control circuit.

Separate sample loops of $5/8$ in. stainless steel tubing constantly circulate fresh materials from the three still overhead lines to a common point about 40 in. from the chromatograph cabinet. Rated pump capacity (Eastern Industries, Hamden, Conn., Model DH-11, Type 100/C99) is 1 gal/min. Upon programmed command, the proper stream is diverted through its solenoid valve into the instrument. While the previous sample is being analyzed, the new stream flushes out the lines in preparation for its own analysis.

To insure fresh sample at the time of injection flow rates of 10 cc/min are used. Correspondingly, dead space and sample volume are kept to less than 15 cc by using miniature inline filters, $1/8$ in. OD sample lines of minimum length and a sample chamber of only 0.2 cc capacity in the injectors. Waste sample flows through a channel common to all three streams and, after passing through a flow meter, is discarded. The sample handling system is pictured in Figure 1.

Each of the three injectors delivers a 3.5 x 10^{-3} cc sample metered by a calibrated undercut in a sample
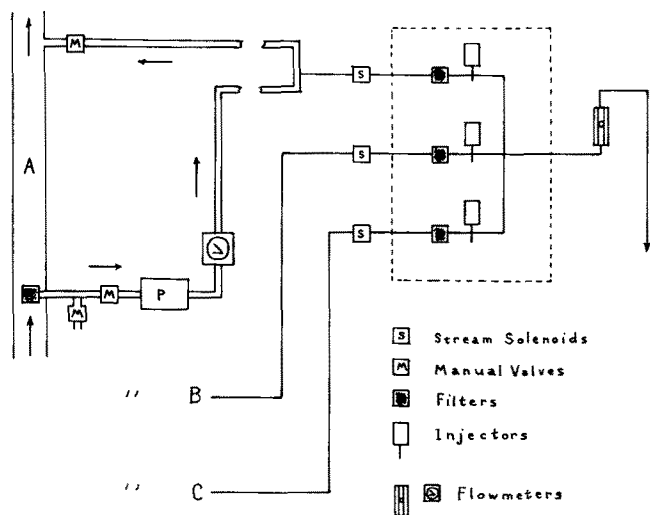
FIG. 1. Sample flow path through process chromatograph.

S	Stream Solenoids
M	Manual Valves
■	Filters
▯	Injectors
S	Flowmeters

metering rod, as shown in Figure 2. Pneumatic action drives this rod downward through a Teflon seal into the detector block. There at a temp of 300C flash vaporization takes place in a stream of helium, and the sample vapors are swept along by the carrier gas into the analytical column.

Programmed Operation

For flexibility the system which effects stream changes is isolated from those which govern the analytical functions of the instrument. However, the op-

FIG. 2. Construction of high temp sample injector.

erations of both are controlled and coordinated by a two-channel tape programmer, which serves as a control center for the analyzer. This unit consists of a 10 ft loop of transparent 16-mm movie film driven by a synchronous motor past a dual cadmium selenide photocell (Clairex CL-604) pickup.

Opaque marks on the upper half of the tape initiate stream changes, while those on the lower half actuate all other functions. Two tape decks are provided, a switching arrangement permitting quick changeover from one program tape to another. Replaceable motors facilitate setting up single or multiple programs of any reasonable length. Provisions are included for handling a total of six streams, and panel switches enable the operator to select those scheduled for analysis.

Marks on the lower half of the tape activate the various analytical circuits by means of a 4-pole 25 contact stepping relay (Rotary Stepping Switch Type 45, Cat. #RW-16V Automatic Electric Sales Corp., Northlake, Ill.). Injection of the sample is initiated by closure of one of these contacts. An electronic timing circuit actuates compressed air solenoid valves which inject the sample and after 10 sec return the metering undercut to the sample chamber. At the same time this circuit locks in an electronic integrator which begins the summation of the total area of the chromatogram.

During the 25 sec preceding the injection of the sample, the recorder pen is automatically zeroed to eliminate any base line drift which may have accumulated during the previous analysis. In practice, no correction is usually required.

As the different components emerge from the column, tape marks timed to coincide with their appearance switch on a peak integrating counter which calculates the area under the individual peaks. At the end of each peak scheduled for printout, a tape marker switches off the digital counter and triggers the printer to stamp out the data. This is repeated for each component of interest; those components of little analytical significance are not scheduled on the program tape, but their areas are included in the total integral data. At the close of the chromatogram, the stepping relay is returned to its home position to await the total printout command. This signal unlocks the total integrator circuit and triggers the printer to print out the total area of all components in the chromatogram. This entire cycle of operation is repeated during each analysis. At each point in the sequence panel lamps indicate which function is being performed and which peak and stream are being analyzed.

Circuit arrangement is such that any malfuctions in the instrument which may cause cumulative program errors are automatically cancelled out when the stepping relay returns to its home position. Only errors in programming and repetitive errors in performance will distrub the normal operating sequence. These errors are easily recognized in the printout data and serve as their own diagnostic indicators in troube shooting the analyzer. The scheduling of a typical program is indicated in Figure 3.

Integration and Readout

Integration of areas under the chromatographic peaks is accomplished by means of a volatage to frequency converter (Magaverter Model FM-2, Pioneer Electronics, Santa Monica, Calif.), which transforms signals from 0–10 v positive into a 12-v square wave of 0–2000 cycles/sec. Linearity of frequency response with volatage input for this unit is within 1%.
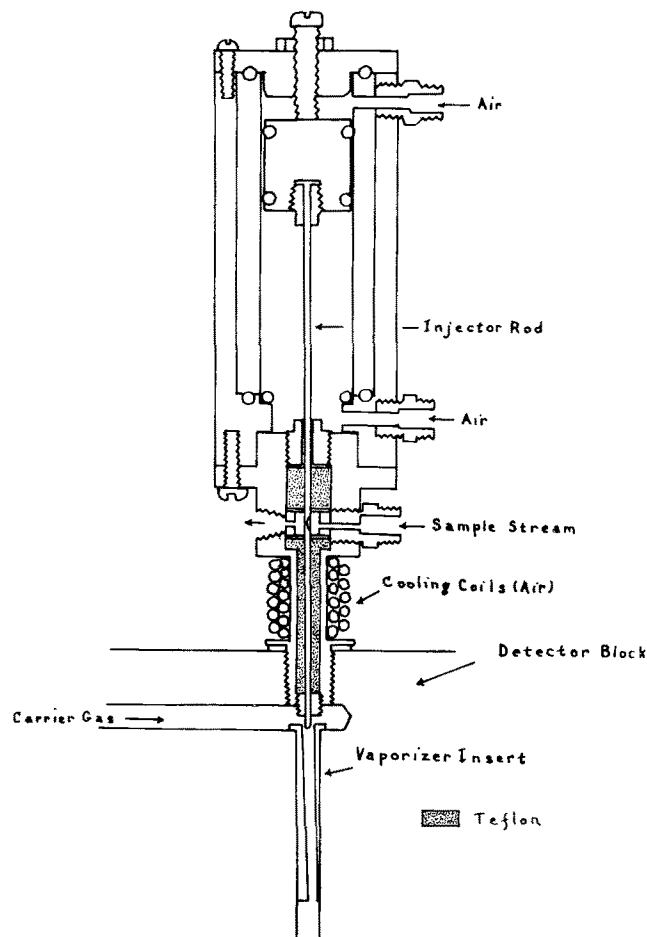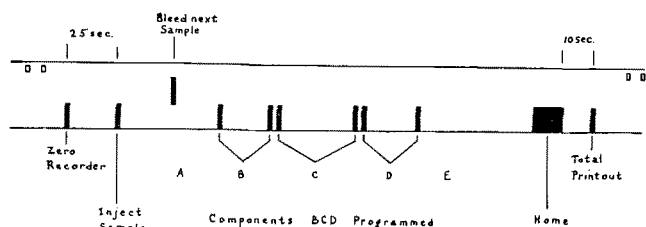
FIG. 3 Typical program tape for five component sample.

The signal fed into the converter is obtained from an anxiliary slide wire in the recorder with a constant potential of ca. 9.5 v applied across its length. This voltage is supplied by a solid state regulated source which is also temp stabilized. Any excursion of the recorder pen above the base line then gives rise to a DC output voltage which is converted into a digital signal directly proportional to the displacement. In normal operation, 10 sec elapse between the injection of the sample and the transfer of the DC signal to the converter. This is to avoid integrating any initial disturbances in gas flow caused by the injection.

The converter input is returned to ground through a second voltage divider in parallel with the slide wire. By varying the position of a tap on this resistor the input signal to the converter may be balanced out and the threshold count set at any convenient level with respect to the base line. The square wave output of the converter is applied either to the total integrating counter alone or to both total and peak integrating modules simultaneously if the component emerging from the column is of analytical interest.

The counting modules, (Burroughs Beam X Counting Decade Module DC-114, Burroughs Corp., Plainfield, N.J.) which incorporate nixie indicating tubes for direct numerical readout, have a maximum counting rate of 10^5 counts/sec, and each bank of 6 modules provides for a total count of 10^6. In normal operation counts seldom exceed 10^5. Some count loss is sustained by the peak counter due to the time required to switch from one peak to another; however, disagreement between peak and total counts is usually less than 0.3%.

To check out the performance of the counting circuits, a test signal of 3600 counts/sec is built in. It consists of a 60-cycle sine wave from the filament supply converted by a Schmitt trigger into a 12-v square wave suitable for driving the voltage to frequency converter.

For obtaining a permanent record of peak areas automatic printout of peak integrals in digital form is included. At the end of each peak programmed and at the end of the complete chromatogram, a signal from the programmer terminates the count and triggers the printer to scan the output circuits of the counters. Here, those target electrodes of the beam switching tubes which have a lower than normal voltage activates the printout of their corresponding digits.

Single and double spacing of data is accomplished by stepping relay circuits, which drive a reversible motor to actuate the spacing bar of the printer. Data from each analysis thus appears as a block of print for each chromatogram. The total integral appears at the head of the column and data for each component of interest is indicated in reverse sequence below it.

The printer (Digital Recorder Model 562A, Hewlett Packard Co., Palo Alto, Calif.) was selected chiefly for its electronic compatibility with the counting modules and also because it can be mounted in a
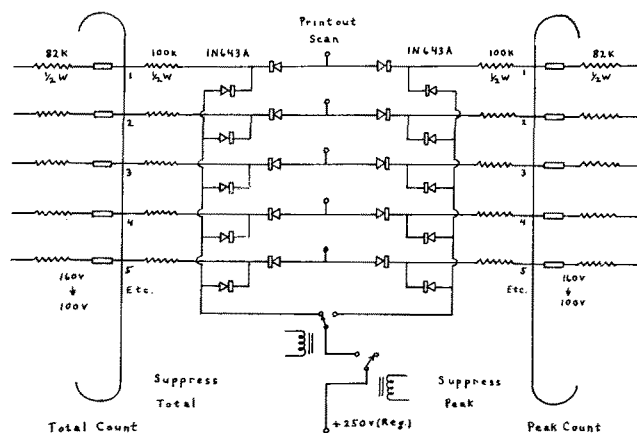

FIG. 4. Diode switching network for printout control.

standard 19-in. rack cabinet. It lends itself readily to the circuit changes which are necessary to incorporate it in the analyzer.

Initially transferring the output of the two banks of counters to the printer input presented a problem. A motor driven 60-pole double throw wafer switch originally constructed was discarded because of its formidable appearance and potential servicing problems. In its place a more reliable solid state diode switching network was devised. This is detailed in Figure 4.

Since the printer responds only to a voltage level considerably lower than its own plate supply voltage, a 250-v potential applied to one bank of beam switching tragets through isolating diodes permits suppression of data from this bank without interfering with the scan of the opposite bank. Actual switching requires only a single pole double throw relay for transferring the diode bias voltage, and the performance of this circuit exhibits the inherent reliability of this device.

Miscellaneous Circuits

The thermal conductivity detector circuit, employing four 20 ohm tungsten Gow Mac filaments is arranged in an opposed bridge circuit to produce twice the normal voltage output. It has excellent thermal stability and has been used in our laboratory instruments over a number of years. A voltage divider based on a 1 : 2 : 5 ratio allows for attenuation of the bridge signal with settings of 1–100x. The recorder, a Westronics Model S-11, is easily adapted to the addition of a zero suppression circuit, automatic zeroing and other changes which were considered desirable. In addition, it mounts compactly in the standard 19-in. rack.
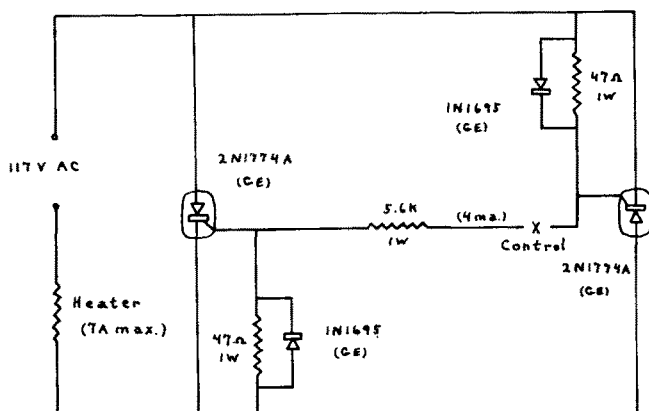

FIG. 5. Silicon-controlled rectifier heat control circuit.

Column temp is controlled by a Simplytrol meter relay which is reset every 30 sec by a motor driven cam. While excellent temp regulation is obtained under fixed ambient conditions, some difficulty has been experienced with temp drift due to the changing temp environment encountered in the chemical plant. The bimetallic element built into these meters is unable to compensate completely for differences in the cold junction potential.

In all circuits where on-off cycling of electrical heaters is required, silicon controlled rectifiers have been employed. The circuit of Figure 5 has been found very satisfactory for these applications (4). The temp of the detector is fixed by a variable voltage transformer, which is protected from line voltage fluctuations by a constant voltage transformer. Any long term temp drift which results in a base line shift of the recorder is compensated for by the automatic zeroing circuits.

Since the solid state components in the counting modules will not function reliably at temp much above 50C, it was necessary to cool the instrument cabinet with a small water-cooled radiator and two 8-in. circulating fans. An air filter and the positive pressure produced by these fans also tend to reduce the amount of dust and grime entering the cabinet.

A simplified schematic of the complete analyzer is shown in Figure 6.

Injector Design

In process chromatography a fundamental problem in encountered in transporting the metered sample to the point where it is to be vaporized. If the path is too long, interfacial contamination from the previous sample becomes objectionable; if it is too short, the volatile materials vaporize in the sample lines, excessive heat conduction causing vapor lock and erratic sample metering.

To avoid these problems without resorting to pressurized sample lines, it was decided to isolate the sample lines thermally from the hot detector block by a path of minimum cross section and of thin-walled stainless steel. For flash vaporization, this requires raising the cool sample rod as well as the sample itself from 80C to ca. 280C within a very few sec. Deterioration of the Teflon packing became evident long before this temp was reached, although the temp actually attained was to low to vaporize the higher boiling fatty acids.

A compromise solution was reached by extending the length of the lower Teflon seal, confining the Teflon with metal to avoid extrusion, raising the detector temperature to 300C or higher, and cooling the Teflon
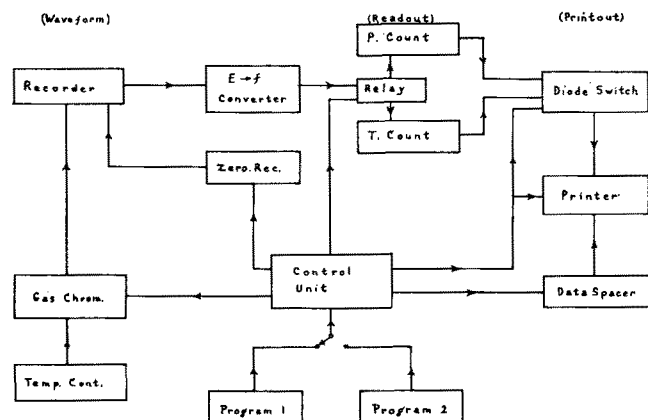
along its length with an air jacket. This construction is detailed in Figure 2. To afford good contact between the sample metering rod and the hot detector wall, an insert with a narrow and slightly oblique channel was provided. The resulting chromatograms indicate little difference between a sample injected manually with a hypodermic syringe and one injected automatically. However, with a single injector inter-

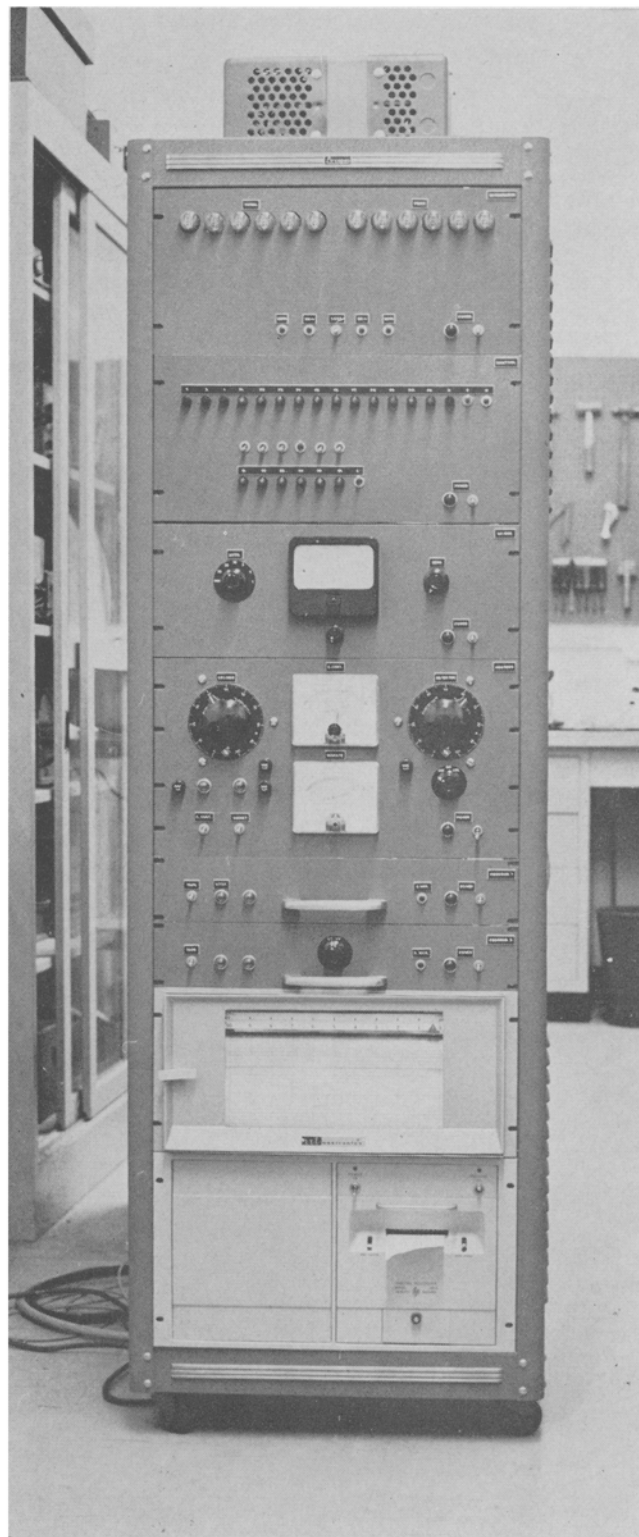FIG. 6. Simplified operational schematic of process analyzer.

FIG. 7. Automatic control console for process instrument. Panels, from top to bottom: Integrator with digital display; control, with stream and peak indicating lamps; detector bridge; temp control; programmer, dual tape decks; recorder and printer.

facial, contamination was encountered along the walls of the Teflon channel through which the metering rod passes. Because this contamination was not eliminated by repeated changes in injector design, the use of three injectors in a series path was adopted. Tailing and other adverse effects due to injection at a point far removed from the column were expected, but have been demonstrated to be nonexistent. The same process stream injected at those points nearest and farthest from the column give chromatograms which may be superimposed.

After its installation in the chemical plant, about six months were required to work out a satisfactory injector design and to eliminate minor irregularities in the overall operation of the analyzer. Since then, the instrument has performed in a very satisfactory manner and its consistently yielding reliable data. The photograph in Figure 7 indicates the general appearance of the automatic control console of the instrument.

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Driers Based on Tall Oil—A Review[1]

ALFRED FISCHER and S. E. HANAN, Nuodex Division, Heyden Newport Chemical Corporation, Elizabeth, New Jersey

Abstract

The metal soaps of tall oil were introduced as paint driers during World War II. Paint industry experience reveals that these oxidation-polymerization catalysts are generally equivalent in performance to naphthenate driers. Physical properties, manufacturing procedures and application of tallate driers in typical paint systems are reviewed.

Introduction

DRIERS ARE MATERIALS which accelerate the hardening of paints, varnishes and related coatings by catalyzing the polymerization and oxidation of the unsaturated oils or alkyds used as film-forming vehicles.

Drying catalysts used at the present time are derived from active drying metals, like cobalt, manganese and lead, and from auxiliary drying metals, like calcium, zirconium, zinc and others.

In order to function as driers, these metals must be converted to compounds possessing good solubility in paint vehicles and having the "right"chemical configuration. Both requirements are important. Compounds, like tetraethyl lead, in which the metal is linked directly to carbon, do not have any catalytic activity although they have the required solubility characteristics. Compounds, like lead stearate, which have the configuration necessary for catalytic activity, function poorly as driers because of their limited solubility in paint vehicles. The drying metal soaps of naphthenic acid, 2-ethylhexanoic acid and tall oil possess both the solubility characteristics and chemical configuration required for good functionality as driers. These metal soaps are the present day driers of commerce.

It is the purpose of this paper to review the properties, methods of manufacture and applications of the tallate driers, i.e., of the drying metal soaps of tall oil.

Tallate driers were introduced during the early stages of World War II. The curtailment of marine shipping of materials of a non-strategic nature was a severe handicap to the paint industry as naphthenic acid is obtained primarily from Eastern European crude oils and Romanian oils, and therefore was in short supply. The coatings industry's concerted effort to obtain a more readily available, economic drier

acid resulted in the commercial utilization of tall oil in the manufacture of driers.

Tallate driers started with the usual cobalt, manganese and lead soaps. As the drier soaps are generally tacky solids, difficult to handle and to incorporate into paints and varnishes, they are supplied as solutions in volatile hydrocarbon solvents at standardized metal contents. Naphthenate driers are standardized at 6% cobalt, 6% manganese and 24% lead metals. These are referred to as a 6,6,24 line of driers. Because of limitations in technology, the first tallate driers contained only 4% cobalt, 4% manganese and 16% lead metals, i.e., a 4,4,16 line.

Advances in the technology of tall oil refining and drier manufacture now make it possible to produce a 6,6,24 tallate line with properties comparable to those of the naphthenates.

Driers based on tall oil are assuming a greater proportion of the total driers used in the industry every year. Although the total poundage of tallate driers has not increased appreciably over the past ten years, the percentage has increased from approx 13% in 1950 to over 25% in 1962. These percentages are based on the total output of tallate and naphthenate driers. The increasing percentage of tallate driers sold, compared to the total usage of driers, may be attributed mainly to two factors. Advances made in the technology of tall oil refining have upgraded the raw material significantly. Increased knowledge of the processes involved in manufacturing driers from tall oil also has contributed to the expanded usage of this product.

Table I shows the approx production in millions of lb of naphthenate and tallate driers for the years 1950 through 1962 (Production of Synthetic Organic Chemicals, U.S. Tariff Commission). The inordinate in-

TABLE I

Year	Production in mm lb		Percentage of production	
	Tallates	Naphthenates	Tallates	Naphthenates
1950	5.0	24.0	17.2	82.7
1951	11.0	17.0	39.3	60.7
1952	5.5	19.0	22.5	77.5
1953	5.5	19.0	22.5	77.5
1954	5.5	19.0	22.5	77.5
1955	5.5	20.0	21.6	78.4
1956	5.0	19.0	22.9	77.1
1957	5.0	21.0	21.2	78.8
1958	6.0	17.0	26.1	73.9
1959	7.0	17.0	29.2	70.8
1960	5.0	15.0	25.0	75.0
1961	7.0	14.0	33.3	66.7
1962	8.0	15.0	35.8	64.2