A Continuous Process for the Dehydration of Castor Oil

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UNTIL comparatively recently castor oil and its derivatives have had only a very limited outlet in the paint and varnish industry for castor oil as such is not a drying oil. About 1937 a synthetic drying oil derived from castor oil by dehydration made its appearance on the market. The growth and use of this new oil has been nothing short of phenomenal, and today dehydrated castor oil ranks as one of the most important drying oils.

The knowledge that ricinoleic acid, the principal constituent of castor oil, could be dehydrated was published in 1888 by Krafft (5). In 1914 Fokin (3) made a systematic study of the dehydration of ricinoleic acid, recognizing the principle of dehydration to give both 9-11 and 9-12 linoleic acids. He also demonstrated that the reesterified acids possessed drying properties. However, not before 1928 were patents filed by J. Scheiber (9) for a process for preparing a drying oil from castor oil by dehydration of the castor fat acids. The Scheiber process was quickly improved upon by Ufer (10), who achieved direct dehydration of the oil. Since then numerous patents have been issued on catalysts for the dehydration of castor oil. However, only a few patents have been granted which represent any great improvement over the original batch method. Semicontinuous processes have been described wherein catalysts are deposited on asbestos or other supports packed in tubes, and the oil is dehydrated by passing it through the heated tubes (1, 8).

Recently, Colbeth (2) obtained a patent on a continuous process embodying the so-called "flash principle," viz., the exposure of thin films of oil to high temperatures for short periods of time, but no details are given on the quality of the product produced.

It was of interest to determine whether castor oil could be dehydrated efficiently by the use of the "flash principle" employing apparatus and conditions other than those previously disclosed and to study the various factors related to the continuous dehydration of the oil.

Experimental

We tested the applicability of the "flash principle" to the dehydration of castor oil by heating thin layers of oil with various catalysts in an apparatus consisting of a heavy walled Erlenmeyer flask with a ground glass joint into which fitted an extra large bore distilling head. Satisfactory dehydrated castor oils were obtained by heating thin layers of the oil in the presence of catalysts under a vacuum of 30 mm. at 300-320°C. for approximately 15 minutes.

Only castor oil soluble catalyst such as phosphoric acid, diethyl sulfate, and concentrated sulfuric acid were evaluated. Concentrated sulfuric acid proved to be the most efficient catalyst tested although it caused considerable darkening of the oil when used in effective concentrations.

This objectionable darkening effect was overcome by diluting the acid with water to a 70-75% concentration. The dilute acid proved to be as effective for dehydration as concentrated acid without causing the objectionable discoloration of the oil. A clear solution of oil and dilute acid result when the mixture is vigorously mixed and allowed to stand a short time.

The apparatus developed for the continuous dehydration is shown in Figure I. Castor oil, containing the desired amount of catalyst, was placed in the separatory funnel (A). The outlet of A was connected to the intake valve of the constant feed pump (Wilson Pulsafeeder, Type VES 144) (B) which controlled the rate of flow. The oil was pumped through ¼-inch Tygon tubing to the top of the dehydration tube (C), which was constructed from a 4-foot stainless steel tube (type 316), ¾ inch in diameter and threaded on the inside (12 threads to the inch). This tube was mounted in a heating jacket made by wrapping 22 feet of Nichrome wire (⅛ inch wide, .010 inch thick, 0.452 ohms/foot) around a 38-mm. I. D. glass tube. An insulating air space was formed by placing a 52-mm. I. D. glass tube over the heating element, and the entire unit was insulated with magnesia lagging.

The oil entering the dehydration tube at the top was distributed around the wall by a fine meshed stainless steel screen cone and was dehydrated as it spiralled down the tube in a thin film. Preliminary work with a dehydration unit made of a glass tube and fitted on the inside with an 18-gauge Nichrome wire coil allowed visual inspection of the dehydration and demonstrated that if the correct number of

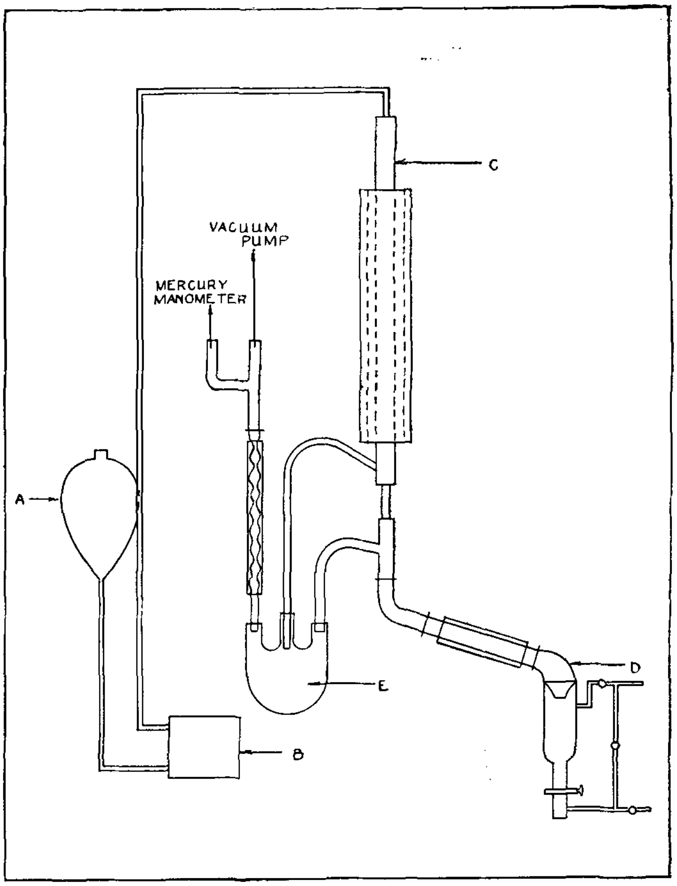

FIG. I.

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turns per inch were used, a moving film of oil covered the entire surface of the tube at all times. Under such conditions local overheating with subsequent polymerization and charring did not occur.

After dehydration the oil was cooled by means of a condenser and collected with the aid of the variable take-off receiver unit (D). The water of dehydration and volatile decomposition products (in gaseous form) were removed at the bottom of the dehydration tube through two exhaust tubes and were condensed and collected in the 3-necked flask (E). The portion not collected by the flask was trapped by the condenser mounted ahead of the vacuum pump.

The vacuum was produced with a water ejector pump, the system being evacuated to approximately 25 mm. absolute pressure. During operation the pressure rose to about 40 mm. due to the pressure created by the water of dehydration and volatile decomposition products produced. Attempts to obtain lower pressures with oil pumps were abandoned because the necessary dry ice traps became blocked early in a run.

The temperature of dehydration was followed with two iron-constantin thermocouples, one placed six inches from the lower end of the dehydration tube and the other at the center of the heating zone of the tube. The lower thermocouple was connected to a Wheelco Capacitrol instrument which controlled the heating element and automatically held the temperature within ± 2°C. Temperatures were checked with a Leeds and Northrup potentiometer. A temperature variation of from 20° to 40°C. existed in all runs between the center and bottom of the dehydration tube.

Acetyl values were determined according to the method of West, Hoagland, and Curtis (11), but using the stronger acetylating solution recommended by Ogg *et al.* (7). Acid values were determined by direct titration of the oil with standard potassium hydroxide solution, and viscosity was obtained by use of a Gardner-Holdt bubble viscometer. Conjugation was measured with a Beckman Quartz Spectrophotometer using Skelly F as the solvent. Since dehydrated castor oil has no triene conjugation, only diene absorption was determined. An $E_{1}^{1\%}$ cm. of 1150 at 2320 Å was taken for 100% diene conjugation.

Drying tests were determined on oils to which 0.2% Pb and 0.04% Co driers had been added. Films were cast on glass plates with a doctor blade, which laid down a wet film thickness of 0.001 inch.

Results and Discussion

The following factors were found to influence the dehydration of the oil: 1. Per cent catalyst, 2. Temperature of dehydration, 3. Rate of flow, 4. Contact time, and 5. Vacuum. These factors were studied in detail using both a 2- and 3-foot heating (dehydrating) zone. Obviously, these factors are closely related, and in some cases, a number of factors were evaluated simultaneously. The effect of these factors was followed by noting the changes of the physical constants of the product. However, the results presented in the tables are given only to indicate the trend or direction of the dehydration with regard to the variable, and they may not necessarily represent optimum conditions. In addition, representative oils were examined for speed of dry.

Per Cent Catalyst. Preliminary experiments indicated that under the conditions listed in Table I as "Factors Held Constant," satisfactory dehydrated oils could be produced. By keeping these factors constant, a study could be made of the effect of catalyst concentration. From the results listed in the table it is evident that as the concentration of the catalyst is increased the resulting oil becomes darker in color. On the other hand, while low concentration of the catalyst produces better colored oils, the product is not as satisfactorily dehydrated as indicated by the acetyl value.[3] For satisfactory results, that is, adequate color and dehydration, a compromise was necessary. For a 2-foot heating zone, a catalyst concentration of 5.5 parts of 73% H_2SO_4 to 1,000 parts of oil was considered best; while with a 3-foot zone a catalyst concentration of 5.0 parts of the acid was best.

TABLE I

Effect of Varying the Percentage Catalyst on the Dehydration of Castor Oil[1]

A. 2-foot heating zone. Factors held constant: (1) Vacuum—35 mm. absolute pressure. (2) Rate of flow—15 ml. per minute. (3) Temperature—324°C.

Catalyst Concentration (Parts of 73% H_2SO_4 per 1,000 of oil)	Ref. Index at 25°C.	Acid Value	Acetyl Value	Percentage Loss	Color (Gardner)	Viscosity
4.0	1.4808	7.5	44.8	......	6	E
4.5	1.4809	9.6	42.0	......	8	E
5.0	1.4811	7.6	36.0	......	9	E
5.5	1.4811	7.6	31.6	......	10	E
B. 3-foot heating zone. Factors held constant: (1) Vacuum—40 mm. absolute pressure. (2) Rate of flow—18 ml. per minute. (3) Temperature—322°C.						
5.0	1.4810	8.4	33.1	7.0	9	E
5.5	1.4811	9.0	29.5	7.3	11	E
6.0	1.4817	8.1	26.2	7.6	14	E

[1] A No. 1 castor oil was used in all experiments. It had the following constants: $n_{d}^{25°} = 1.4772$, acetyl value = 156.8, and acid value = 2.6.

Temperature and Rate of Flow. These two factors are very closely related to one another in that the higher the temperature of dehydration, the higher the rate of flow necessary to avoid excess cracking of the oil resulting in high acid values and high decomposition losses. The effect of these two factors are shown by the results listed in Table II.

Contact Time. The estimated contact times for the various rates of flow varied from 14 seconds to 25 seconds for the 2-foot heating zone and from 21 seconds to 37 seconds for the 3-foot zone. These values were obtained from calculations by assuming that the thickness of the film was equal to the depth of the thread (.054 inches). The volume of oil being heated at any one time was therefore 5.0 ml. for a 2-foot zone and 7.5 ml. for a 3-foot zone. If, for example, the rate of flow through a 2-foot zone was 12 ml. per minute, then the contact time would be:

$$60 \times \frac{5}{12} = 25 \text{ seconds.}$$

It must be recognized that these values are probably too high, especially at higher rates of flow, since some of the oil passes over the threads and cascades down the tube.

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[3] Our acetyl values were somewhat greater than most of the commercial oils examined (see Table VI). These higher values may be caused by poorer dehydroxylation; however, another possible explanation is that the very short processing times does not allow the free acids which are formed to react with hydroxyl groups as is possible in the batch process.

TABLE II

Effect of Temperature and Rate of Flow on the Dehydration of Castor Oil[1]

	Temp. °C.	Ref. Index at 25°C.	Acid Value	Acetyl Value	Temp. °C.	Ref. Index at 25°C.	Acid Value	Acetyl Value
	Rate 12 ml. per minute				Rate 15 ml. per minute			
2-Foot Heating Zone[2]	311	1.4811	7.8	30.3	314	1.4811	6.7	34.6
	324	1.4811	8.8	29.5	323	1.4811	7.8	34.0
	334	1.4815	10.3	28.6	334	1.4813	6.8	30.1
	345	1.4815	12.3	29.1	346	1.4814	7.8	31.8
3-Foot Heating Zone[3]	311	1.4803	9.7	24.0	310	1.4811	8.5	30.5
	318	1.4807	9.5	27.9	322	1.4810	10.2	30.2
	322	1.4808	11.5	28.6	333	1.4811	12.6	29.8
	327	1.4809	13.0	27.8	344	1.4813	15.7	30.2
	Rate 18 ml. per minute				Rate 21 ml. per minute			
2-Foot Heating Zone[2]	313	1.4809	5.4	38.8	313	1.4808	5.1	38.4
	321	1.4811	6.2	34.8	322	1.4811	5.6	36.4
	336	1.4812	7.2	33.4	334	1.4811	6.3	36.3
	346	1.4812	8.6	32.2	343	1.4811	7.0	36.8
3-Foot Heating Zone[3]	310	1.4809	7.6	33.5	310	1.4808	6.4	39.4
	320	1.4810	8.4	33.1	320	1.4810	7.4	35.3
	333	1.4811	10.2	33.2	333	1.4810	8.5	35.3
	343	1.4811	12.1	33.2	343	1.4811	10.7	38.0

[1] The viscosities of all the dehydrated oils were about an E.

[2] Factors held constant: (1) Vacuum—34 mm. absolute pressure. (2) Catalyst concentration—5.5 parts of 73% H_2SO_4 per 1,000 parts of oil.

[3] Factors held constant: (1) Vacuum—approximately 10 mm. absolute pressure. (2) Catalyst concentration—5 parts of 73% H_2SO_4 per 1,000 parts of oil.

These short contact times account for the low viscosity of the dehydrated oils produced, 1.25 poises at 25°C. (E on the Gardner-Holdt Scale). Although the temperature of dehydration is quite high, the oils are not held at these temperatures long enough for any significant amount of polymerization to occur.

Vacuum. The effect of vacuum on the dehydration of castor oil is shown by the data in Table III. These data show that the lower the pressure, the lower the acetyl value of the oil, indicating better dehydration. However, the color of the oil varies inversely with the pressure; that is, at lower pressures darker colored oils are produced. This effect was attributed to the increased effectiveness of the catalyst with decreased pressure since better dehydration was obtained as indicated by the acetyl value.

TABLE III

Effect of Vacuum on the Dehydration of Castor Oil

Factors held constant: (1) 2-ft. Heating Zone. (2) Temperature—323°C. (3) Catalyst Concentration—5.5 parts of 73% H_2SO_4 per 1,000 parts of oil.

Vacuum (mm.)	Ref. Index at 25°C.	Acid Value	Acetyl Value	Percentage Loss	Viscosity
35	1.4811	7.7	32.2	8.2	E
60	1.4812	9.1	33.4	7.9	E
80	1.4810	8.3	39.4	7.2	E
100	1.4810	10.2	36.7	7.1	E

Decomposition Losses. The decomposition losses on dehydration of castor oil can be divided into two parts. One part consists of the water formed by dehydration and theoretically amounts to approximately 5% of the total weight of the starting oil. The other part consists of those losses due to cracking of the oil. Obviously, losses due to dehydration cannot be avoided if a desirable product is to be obtained, but other decomposition losses are to be prevented if possible.

Decomposition losses at various rates of flow at a constant temperature are given in Table IV. These values are so close that differences may be considered as due to experimental error and hence indicate that the rate of flow at constant temperature has little or no effect on the total amount of decomposition. However, decomposition losses are affected by changes in vacuum as indicated from the data in Table III. Although there is an increase in the losses as the pressure is lowered, this may be attributed to more effective dehydration and improved removal of decomposition products. Decomposition losses are also related to the amount of catalyst employed as shown by the data in Table I. Increasing the catalyst would tend to produce more effective dehydration and possibly tend to increase undesirable side reactions.

TABLE IV

Percentage Loss of Dehydrated Castor Oil at Various Rates of Flow[1]

Conditions: (1) 3-ft. heating zone. (2) Vacuum—40 mm. absolute pressure. (3) Temperature—320°C. (4) Catalyst Concentration—5 parts of 73% H_2SO_4 per 1,000 parts oil.

Rates of Flow (ml. per minute)	Ref. Index at 25°C.	Acid Value	Acetyl Value	Viscosity	Percentage Loss
12	1.4811	10.8	29.0	E	6.8
15	1.4811	9.3	30.0	E	7.0
18	1.4810	8.4	32.1	E	6.9
21	1.4811	6.8	36.0	E	7.0

[1] About 1,450 gm. of oil was used per run.

Evaluation of Oils. According to von Mikusch (6) and Greaves (4), performance tests are the best way of evaluating a dehydrated castor oil. They both agree that one of the best single tests is the speed of dry. Drying times were determined on representative dehydrated oils to study the effect of the various processing conditions and physical properties of the product on this important performance characteristic. In Table V the effect on temperature, rate of flow,

TABLE V

Effect of Certain Variables on the Drying Time of Dehydrated Castor Oils

Factor Held Constant	A. Temperature °C.	Acetyl Value	Acid Value	Percentage Diene Conjugation	Set-to-touch Time
See Table II 3-ft. Heating Zone Rate–15 ml./min.	310	30.5	8.5	31.5	2′ 20″
	322	30.2	10.2	28.4	2′ 0″
	333	29.8	12.7	30.8	2′ 25″
	344	30.2	15.8	30.8	1′ 17″
See Table II 3-ft. Heating Zone Temp.–322°C.	B. Rate of Flow (ml. per min.)				
	12	29.0	10.8	30.1	2′ 15″
	15	30.0	9.3	30.0	3′ 5″
	18	32.0	8.4	28.5	2′ 25″
	21	.36.0	6.8	29.7	2′ 30″
See Table I 2-ft. Heating Zone	C. Parts of 73% H_2SO_4 per 1,000 parts of oil				
	4.0	44.8	7.5	23.8	3′ 0″
	4.5	42.0	9.6	24.7	2′ 30″
	5.0	36.0	7.6	20.1	2′ 30″
	5.5	31.6	7.8	31.0	2′ 45″

TABLE VI

Properties of a Few Representative Dehydrated Castor Oils

	Ref. Index at 25°C.	Acid [1] Value	Acetyl Value	Viscosity (Gardner-Holdt)	Color [2] (Gardner)	Percent Diene Conjugation	Set-to-touch Time
Commercial (1)	1.4808	5.8	42.1	G+	6	26.8	2′ 30″
Commercial (2)	1.4813	3.3	22.9	G	4	26.3	1′ 45″
Commercial (3)	1.4809	4.1	25.3	G	5-6	27.0	1′ 45″
Commercial (4)	1.4809	4.8	28.3	I	7-8	23.8	2′ 5″
Continuous (1)	1.4812	8.6	32.2	E	7	31.5	1′ 55″
Continuous (2)	1.4815	10.3	28.6	E	9	29.2	2′ 15″

[1] The acid values of our dehydrated oils are high, possibly because of the poor vacuum employed.

[2] The Gardner color values must be taken with reservation as some of the oils could not be accurately matched with the standards.

acetyl value, and per cent conjugation on the drying time of the representative oils is given. It is evident from these results that there is little or no correlation between the various factors and drying time.

A comparison was made of the properties of two oils dehydrated continuously with several commercial dehydrated castor oils. The results are given in Table VI. In addition, 54-gallon Limed Rosin varnishes were prepared from these oils. In general, only slight differences were detected among the set-to-touch times, hot and cold water, and alkali resistance. However, the varnishes prepared, using the continuously dehydrated oils, produced significantly harder films.

Summary

A process for dehydrating castor oil continuously has been presented. The method consists essentially of exposing the oil in a thin film under the vacuum to temperatures between 310° and 350°C. for short periods of time in the presence of a dilute sulfuric acid catalyst. The relationship between various operational conditions and the physical constants of the oil produced has been determined. In addition, the oils were compared with several representative commercial oils.

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Report of the Color Committee

Spectrophotometric Color Grading

Review of Previous Work

DURING the past several years the situation with respect to obtaining Lovibond type color glasses has grown steadily worse. On December 12, 1947, A. J. Fawcett, in a letter to R. R. King, writes, "we are therefore advising our U.S.A. customers that we regret we must cancel all orders outstanding on our books for loose glasses." This final word puts it squarely up to the committee to eliminate once and for all the Lovibond system for measuring oil colors, especially where grading for trading purposes is involved. The Lovibond system has served a useful and needed purpose but, as tools, visual colorimeters using Lovibond color glasses are outmoded by the recent advances in scientific instruments. Past reports of the Color Committee have indicated that photoelectric colorimeters can be used successfully to grade oils and, where necessary, a translation to Lovibond red colors can be accomplished. There are certain drawbacks to any scientific instrument, and in the past cooperation of instrument makers with the Color Committee has left much to be desired. Hence no specific recommendation has been made by the Color Committee since it has felt that no well standardized filter-photocell instrument was available on the market.

During the past year or two there has been a decided tendency toward the use of a spectrophotometer for measuring oil colors. This is because the spectrophotometer produces fundamental data amenable to all sorts of color analyses. The development of simple, photoelectric instruments, which are easy to manipulate as well as inexpensive, has also been a decided factor in extending the use of spectrophotometers in color measurements. It is the purpose of this report to present some of the data relative to oil colors which has been obtained by using the Coleman Model 6A spectrophotometer and to suggest a method whereby spectrophotometric data may be used to replace all measurements now made using the Lovibond system. It is hoped that additional cooperative work will lead to a finished method that will be adopted by the Uniform Methods Committee of the Society.

Work Done

A recent model Coleman spectrophotometer, 6A Junior, was obtained from Coleman Instruments inc. Mr. Coleman points out that he is desirous of cooperating in every way with the committee in the design of the instrument, furnishing any number of instruments for committee use, and standardizing the instruments to committee specifications when and if such a time should come. This is an important point and well worth consideration in investigating any new instrument for use in widely different laboratories. Two companies, Swift and Company and Archer-Daniels-Midland, have had considerable experience with the Coleman spectrophotometer and have found the instruments quite satisfactory from an operation standpoint. These instruments are simply