Kirk-Othmer Encyclopedia of Chemical Technology.

CASTOR OIL

Castor oil [8001-79-4] is derived from the bean of the castor plant *Ricinus communis*, belonging to the family Euphorbiaceae. The castor bean is not a legume as the name implies but is a member of the spurge family. Castor plants occur in practically all tropical and subtropical countries. They are also grown annually from seed as both ornamental and cultivated plants in temperate zones. There are wide variations in the size, form, and color of the plant, as well as the size and color of the seed. Colors vary from extreme red to pure green and the stems, leaves, and fruits are covered to a varying extent by a waxy, bluish bloom. The usually three-seeded capsules may be spiny and display great variety in size, shape, and color patterns. There is, however, relatively little variation in the oil content of the fully matured seeds and in the chemical composition of the oil derived therefrom (1, 2).

The seeds of the castor plant are produced in racemes, or clusters of capsules. The capsules each contain three seeds protected by a hull that is removed prior to processing. The seeds are mottled to varying extents, most often with shades of dark brown overlaying shades of light brown. Seeds of commercial varieties range from 250 to 1800/kg. The seeds are toxic, and the ingestion of several seeds can be fatal to humans.

Whereas commercial production of castor oil existed in the United States in the 1800s, production shifted to tropical and subtropical countries in the early 1900s. World War I, World War II, and the Korean conflict each influenced efforts to produce hybrid castor species and increase U.S. planting, and by the late 1960s, approximately 80,000 acres of castor were grown in the United States producing 29,500 metric tons of castor oil. U.S. production was competitive until 1972 when Federal price supports were withdrawn. U.S. production dropped almost to zero by 1974.

Interest in the restoration of U.S. castor seed production was initiated in 1989. An aggressive hybrid seed program was developed in Texas (3), and sufficient hybrid seed was grown in 1990 to plant 40,000 acres of castor in 1991. Mechanization of harvesting equipment for the collection of dwarf (~ 1 m) hybrid plants retaining the seed pods on the plant until harvested, was expected to yield from 800–900 kilograms of seed per acre. Although the U.S. Department of Defense continues to classify castor derivatives as a critical strategic material, in 1990, the United States imported 100% of its castor oil needs primarily from Brazil and India. Furthermore, fluctuating supplies and prices of imported oil fostered the use of alternative feedstocks (see Chemurgy).

1. Properties

Castor oil is also known as ricinus oil, oil of Palma Christi, tangantangan oil, and neoloid. Typical of vegetable oils and most fats, castor oil is a triglyceride of various fatty acids (see Fats and fatty acids.) Its uniqueness stems from the very high (87–90 wt %) content of ricinoleic acid, $C_{18}H_{34}O_3$, structurally *cis*-12-hydroxyoctadeca-9-enoic acid, $CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7COOH$, an eighteen-carbon hydroxylated fatty acid having one double bond. Castor oil, sometimes described as a triglyceride of ricinoleic acid, is one of the few commercially available glycerides that contains hydroxyl functionality in such a high percentage of one fatty acid.

Table 1. Fatty Acid Composition of Castor Oil

Fatty acid	CAS Registry number	Molecular formula	Wt %[a]
ricinoleic acid	[141-22-0]	$C_{18}H_{34}O_3$	89.5
dihydroxystearic acid	[26248-43-1]	$C_{18}H_{36}O_4$	0.7
palmitic acid	[57-10-3]	$C_{16}H_{32}O_2$	1.0
stearic acid	[57-11-4]	$C_{18}H_{36}O_2$	1.0
oleic acid	[112-80-1]	$C_{18}H_{34}O_2$	3.0
linoleic acid	[60-33-3]	$C_{18}H_{32}O_2$	4.2
linolenic acid	[436-40-1]	$C_{18}H_{30}O_2$	0.3
eicosanoic acid	[506-30-9]	$C_{20}H_{40}O_2$	0.3

[a] These are typical values.

Table 2. Industrial Castor Oil Standards[a]

Property	Value
acid value, max	2.0
clarity	clear
Gardner color, max	2
hydroxyl value	160–168
loss on heating, wt % max	0.2
refractive index, 25°C	1.4764–1.4778
saponification value	176–184
solubility in alcohol[b]	complete
specific gravity, 25/25°C	0.957–0.961
unsaponifiable matter, wt % max	0.7
viscosity, mm^2/s (=cSt)	6.50–8.00
iodine value	84–88

[a] Ref. 5.
[b] Soluble 1:2 by vol in 95% ethanol at 20°C.

The average fatty acid composition of castor oil is given in Table 1 (4). Castor oil, is the only significant oil composed mainly of the glyceride of a hydroxylated fatty acid. Ricinoleic acid has an acid value of 180, a saponification value of 186, a Wijs iodine value of 89, and a melting point of 5.5°C. The 12th carbon is asymmetric, resulting in an optical rotation of $[\alpha]_D^{22} = 6.67$. Other ricinoleic acid properties are Gardner color 5; viscosity at 25°C, 400 mm^2/s (=cSt); pour point, $-23°C$; specific gravity at 25°C, -0.940; index of refraction at 25°C, 1.4699. Ricinoleic acid cannot be distilled unless special precautions are taken via derivative formation to protect the hydroxyl group.

Standards for industrial quality castor oil as specified by the ASTM are given in Table 2, and other general properties of castor oil are listed in Table 3.

Castor oil is distinguished from other triglycerides by its high specific gravity, viscosity, and hydroxyl value. Another unique feature is alcohol solubility: one volume of castor oil dissolves in two volumes of 95% ethyl alcohol at room temperature, and the oil is miscible in all proportions with absolute ethyl alcohol. Also the oil is typically soluble in polar organic solvents and less soluble in aliphatic hydrocarbon and other nonpolar organic solvents. Its slight solubility in petroleum ether is a characteristic distinguishing it from other fats. The oil can vary in color depending on the method of recovery and blending to meet specifications. Normally, it is pale yellow, highly viscous, and has a slight characteristic odor. Although it is nearly tasteless, its minor use as a cathartic agent has earned it an unenviable reputation.

Table 3. Properties of Castor Oil

Property	Value
viscosity,[a] 25°C, mm^2/s(=cSt)	615–790
flash point, Cleveland open cup, °C	285
tag closed cup	230
surface tension, mN/m	39.0
20°C	39.0
80°C	35.2
Reichert-Meissl value	<0.5
Polenske value	<0.5
acetyl value	144–150
optical rotation (polarimeter, 200 mm)	+7.5 – 9.0
pour point, °C	−23
coefficient of expansion, mL/°C	0.00066

[a] Value corresponds to $U \pm \frac{1}{2}$ in Gardner-Holdt units (see Rheological measurements).

Table 4. Castor Oil Quality and Specifications[a]

Property	Pale oil	No. 1 oil	No. 2 oil	No. 3 oil
color, AOCS[b,c] tintometer,	10 yellow/1.0 red	20Y/2.0R	30Y/3.0R	40Y/4.0R
free fatty acids,[c] wt %	0.75	1.00	1.50	3.0
acid value,[c]	1.49	1.99	2.98	5.97
moisture and volatiles,[c] wt %	0.255	0.355	0.485	0.485
water content,[c] (Karl Fischer), wt %	0.25	0.35	0.48	0.48
insoluble impurities,[c] wt %	0.01	0.02	0.02	0.2
appearance, 25°C	brilliantly clear; free of suspended matter	characteristically clear; free from suspended matter	characteristically clear; and free from suspended matter	not exceeding slight haze; free of suspended matter
odor	very slight; characteristic	slight; characteristic	slight; characteristic	characteristic

[a] All oil has viscosity in the 680–900 mm^2/s (=cSt) range, equivalent to a U-V classification in Gardner-Holdt units.
[b] AOCS = American Oil Chemists Society.
[c] Values given are maximum allowable.

2. Quality and Specifications

The quality of various grades of castor oil have been prescribed by the International Castor Oil Association, Inc. (ICOAI). Specifications prescribed for the triglyceride oil derived from a plant of the genus *Ricinus communis* are shown in Table 4. The International Castor Oil Association, Inc. has also established chemical properties to be used in the event of a dispute between buyer and seller as to the purity of the oil. These specifications are given in Table 5.

3. Oil and Meal Recovery

The commercial process for castor oil recovery from the seed consists of preheating the seed in stack cookers prior to crushing in a hydraulic press or a continuous mechanical screw-type press commonly known as an expeller. The presscake discharged from this mechanical processing contains 10–20 wt % oil and is then

Table 5. Commercial Castor Oil Specifications

Property	Pale pressed and No. 1 oils	No. 2 and No. 3 oils	AOCS test method[a]
specific gravity, at 25°C	0.955–0.965	0.950–0.965	Cc 10–25
refractive index at 25°C, n_D	1.476–1.479	1.475–1.480	Cc 7–25
acetyl value,[b]	142	140	Cd 4–40
iodine value	82–88	80–88	Cd 1–25
saponification value	176–184	174–184	Cd 3–25
unsaponifiable matter,[c] wt %	0.7	0.8	Ca 6a–40

[a] AOCS = American Oil Chemists Society.
[b] Minimum value given.
[c] Maximum value given.

processed in solvent extraction units to recover the residual oil. Cold-pressing of castor seed that has not been preheated is still carried out to a limited degree in castor growing countries such as Brazil and India. A light colored, high quality medicinal type oil is recovered. Castor oil recovered from hydraulic or continuous mechanical screw presses requires refining to remove toxic proteins, gums, and foreign matter while improving the color and reducing the free fatty acid content.

Solvent extraction in batch or continuous systems is used to recover most of the residual oil from the presscake. Heptane, hexane, or a mixture of these solvents is used to recover the oil. The solvent-extracted presscake is steam stripped to recover solvent and a residual meal known as castor pomace, containing 1% residual oil. The solvent extracted oil is also processed for solvent recovery (qv). The oil from the extraction procedure is darker than the mechanically pressed oil and has a higher free fatty acid content. It is sometimes referred to as a No. 3 castor oil and is used for blending with higher quality oils that are well above No. 1 specifications.

The castor pomace has a protein content of approximately 35 wt % and is used predominantly as an organic fertilizer for slow release of nitrogen. It has not been used extensively as an animal feed supplement because of the presence of toxins and allergens (6, 7). Castor pomace typically analyzes as: 48 wt % carbohydrate, 36 wt % protein, 9 wt % moisture and volatile material, 6 wt % ash, and 1 wt % oil. The castor protein contains a poisonous, but heat labile protein called ricin and a toxic alkaloid known as ricinine and must be further processed. The ricin, present in relatively large amounts, can be easily destroyed by steam heat used in evaporating solvent from the extracted meal. The ricinine, present in small amounts, is not considered significantly detrimental (8). Of primary concern, however, is the presence of a very potent and heat-resistant allergen known as CB-1A. Allergen levels as high as 7 to 12.5 wt % have been recorded for castor; usual levels are 0.7 to 1.5 wt % in the meal before treatment (9–14).

A castor meal treating program for simultaneous detoxification and deallergenation led to the development of a process to detoxify the meal by heat and moisture and to deallergenate by chemical and water treatment utilizing expander/extruder processing techniques (14). This detoxified and deallergenated castor meal is safe to use as feed for animals (see Feeds and feed additives).

A commercial plant in Thailand successfully treats castor meal at a rate of 3 t/h. The typical amino acid wt % analysis of castor pomace important for livestock rations is methionine 1.5%; threonine, 3.6%; valine, 6.6%; leucine and isoleucine, 12.5%; phenylalanine, 4.2%; tyrosine, 3.2%; proline, 3.9%, aspartic acid, 4.6%; glutamic acid, 18.0%; tryptophane, 0.8%; arginine, 16.0%; lysine, 3.1%; histidine, 2.5%; and other nitrogen compounds, 19.5%. Spectrographic analysis of castor pomace yields wt % values of Ca, 0.35; Mg, 1.17; S, 0.34; Mn, 0.012; Fe, 0.22; Cu, 0.007; B, 0.004; Zn, 0.005; and Mo, 0.0003. Wet analysis shows 1.65 wt % phosphoric acid, P_2O_5 total, and 1.10 wt % water-soluble potash, K_2O. This detoxified, deallergenated meal produced in Thailand is undergoing animal-feed testing. Treated castor meal produced in Texas during 1960–1970 was successfully used in cattle rations. The sales of treated castor meal for animal feeding are expected to play a significant role in stabilizing the price of castor oil.

The recovery of oil to meet specifications of the ICOAI for better quality oils requires four processes:

3.0.0.1. Degumming. The oil and dissolved and dispersed proteinaceous materials are treated with 3–5 wt % water at a temperature of 70–80°C and passed through a decanter-type centrifuge to separate the gums from solation. Decanter-type centrifuges are virtually a necessity for this operation and a combination of a dry degumming agent and a solids handling decanter offer the most effective first-stage processing of the oil.

3.0.0.2. Removal of Free Fatty Acids. Alkali treatment of the oil is accomplished by the use of caustic soda solutions to neutralize the excess free fatty acids. Because castor oil readily forms emulsions with water and/or alkaline solutions, special techniques have been developed to neutralize the acids. A continuous counter-current process was developed using a stationary contact reactor (15). Treatment in the presence of a solvent is also utilized (16).

3.0.0.3. Deodorization. Volatile components present from the processing of castor seed to recover the oil are removed by nitrogen or steam stripping operations. Typical steam stripping is carried out at 160°C under less than 1.5 kPa (11 mm Hg) pressure. Processes have been developed for efficient steam–oil contact (17). A unique method of contacting the oil and steam using closely spaced plates to form vertical channels arranged in sequence has been developed. The sparge steam is injected at the base of the channel, and its expansion, as it leaves the sparge holes, throws the hot oil onto the plates as a film. The oil film is dragged to the top of the plate and to the base of the next channel where the process is repeated with fresh steam injections. The steam and stripped volatiles continue up and out of the stripping zone while the turbulent flow regime in the oil phase overcomes the liquid-phase diffusion of the volatile materials. This thin-film steam stripper exposes the oil to high temperatures for a minimum time span of approximately 20 minutes. Steam refining of castor oil using this process at 230°C under vacuum produces a light colored product and very low, free fatty acid content (18, 19)

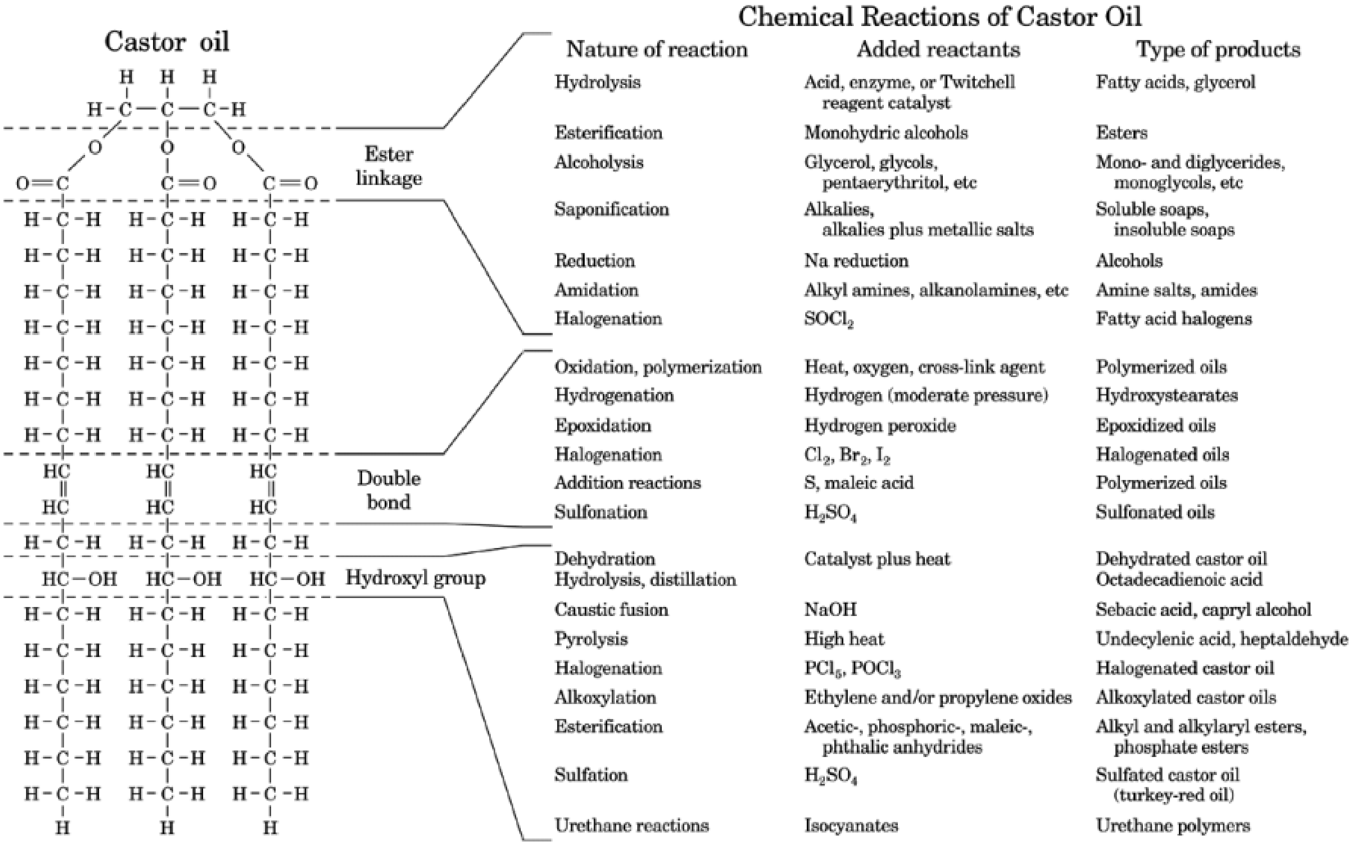
3.0.0.4. Decolorization. The decolorizing or bleaching of castor oil differs from the bleaching of most other vegetable oils because castor oil contains so much 12-hydroxy-9-octadecenoic acid. Castor oil bleachability varies depending on whether the oil is from pressed or extracted sources. The temperature, time of bleaching, and type of activated clays (qv) used all affect the results. At higher (110°C) temperatures, ricinoleic acid is partly dehydrated to 9-11-octadecadienoic acid, and hydroperoxide decompositions resulting in an increase of conjugated dienes. When such reactions occur, the hydroxyl value is lowered because of the formation of water and keto compounds. The use of acid activated clays at a level of 1–2 wt % at temperatures of 80°C and under a vacuum of 1.5 kPa has been found to be effective in giving pronounced color improvement of mechanically pressed oil. The use of 0.5 to 1.0 wt % of activated carbon added to the activated clay has been effective when treating darker colored oils.

4. Chemical Reactions

Castor oil serves as an industrial raw material for the manufacture of a number of complex organic derivatives (20, 21). Chemical reactions occur at the three basic points of functionality as shown in Figure 1.

4.1. Dehydration

Catalytic dehydration converts the nondrying castor oil to an excellent drying oil called dehydrated castor oil [64147-40-6] used extensively by the coatings (qv) industry. Commercial application of this material became significant during World War II in making a tung oil replacement. In the dehydration reaction, the hydroxyl group at the 12th position of the ricinoleic acid is removed along with a hydrogen atom from the 11th or 13th carbon atom to form water and a new double bond (22).



Chemical Reactions of Castor Oil

Nature of reaction	Added reactants	Type of products
Hydrolysis	Acid, enzyme, or Twitchell reagent catalyst	Fatty acids, glycerol
Esterification	Monohydric alcohols	Esters
Alcoholysis	Glycerol, glycols, pentaerythritol, etc	Mono- and diglycerides, monoglycols, etc
Saponification	Alkalies, alkalies plus metallic salts	Soluble soaps, insoluble soaps
Reduction	Na reduction	Alcohols
Amidation	Alkyl amines, alkanolamines, etc	Amine salts, amides
Halogenation	$SOCl_2$	Fatty acid halogens
Oxidation, polymerization	Heat, oxygen, cross-link agent	Polymerized oils
Hydrogenation	Hydrogen (moderate pressure)	Hydroxystearates
Epoxidation	Hydrogen peroxide	Epoxidized oils
Halogenation	Cl_2, Br_2, I_2	Halogenated oils
Addition reactions	S, maleic acid	Polymerized oils
Sulfonation	H_2SO_4	Sulfonated oils
Dehydration Hydrolysis, distillation	Catalyst plus heat	Dehydrated castor oil Octadecadienoic acid
Caustic fusion	NaOH	Sebacic acid, capryl alcohol
Pyrolysis	High heat	Undecylenic acid, heptaldehyde
Halogenation	PCl_5, $POCl_3$	Halogenated castor oil
Alkoxylation	Ethylene and/or propylene oxides	Alkoxylated castor oils
Esterification	Acetic-, phosphoric-, maleic-, phthalic anhydrides	Alkyl and alkylaryl esters, phosphate esters
Sulfation	H_2SO_4	Sulfated castor oil (turkey-red oil)
Urethane reactions	Isocyanates	Urethane polymers

Fig. 1. Structure and reactivity of castor oil.(Courtesy of CashChem, Inc.)

Analyses of commercial dehydrated castor oil indicate that using sulfuric acid as the catalyst, about 30% of the linoleic acid double bonds are in the conjugated 9,11 position. Practical dehydration processes improve color, reduce the after-tack after drying, and increase conjugation. The most common dehydration catalysts are sulfuric acid and its acid salts (23), oxides (24, 25), and activated earth (26). The viscosity of the product is regulated by the degree of dehydration, reaction time, and temperature. Properties of two commercial-grade dehydrated castor oils are shown in Table 6. Systems for continuous dehydration have been patented (28, 29). Dehydrated castor oil is well known for its nonyellowing film formation, outstanding color retention, and flexibility and adhesion in protective coatings (30).

The dehydrated castor oil fatty acids [61789-45-5] are obtained by hydrolysis or by saponification followed by acidification of the dehydrated oil. The conjugated acid content of the product remains the same as in the oil itself. Much higher, 50 wt % and above, conjugated acid contents are obtained by dehydration of ricinoleic acid (31). Usually, the crude acids are distilled under vacuum to obtain a light colored, high quality product. Properties of dehydrated castor acids are shown in Table 7. Type I is distilled grade; Type II is crude, undistilled grade acid.

Table 6. Dehydrated Castor Oil Specifications[a]

Parameter	Unbodied oil[b]	Bodied oil[b]	ASTM method
viscosity at 25°C, $mm^2/s(=cSt)$	140–225[c]	3,800–6,500[d]	D1545, D445
specific gravity, 25/25°C	0.926–0.937	0.944–0.966	D1963, D1475
acid value	6	6	D1639
saponification value	188–195	188–195	D1962
iodine value (Wijs)	125–145	100 min	D1959
color number (Garnder)	5	7	D1554
gel time at 315°C, min	145	63	D1955
set-to-touch time, h	2.5	1.4	
refractive index at 25°C	1.4805–1.4825	1.4860–1.4890	

[a] Ref. 27.
[b] Bodied refers to polymerized castor oil of higher viscosity; unbodied refers to dehydrated castor oil that has not been additionally heat polymerized.
[c] Corresponds to F-I designation in Gardner-Holdt units.
[d] Corresponds to Z2–Z4 designation in Garden-Holdt units.

Table 7. ASTM Requirements for Dehydrated Castor Acids[a]

Requirement	Type I	Type II	ASTM method
acid value	195–200	187–195	D1980
saponification value	195–200	193–199	D1962
iodine value	150–156	138–143	D1959
color (Gardner)	1 max	5–8	D1544
spectrophotometric diene value	28–35	25–32	D1358

[a] Ref. 32.

4.2. Sulfation

Sulfated castor oil, also known as turkey-red oil, represents one of the earliest chemical derivatives of castor oil. The traditional method of preparing turkey-red oil is to add concentrated sulfuric acid at a controlled rate to castor oil over a period of several hours with constant cooling and agitation of the reaction mass to maintain a temperature of 25–30°C. After acid addition is complete, the reaction mass is washed then neutralized using an alkali solution or an amine.

Castor oil sulfation results largely in a sulfuric acid ester in which the hydroxyl group of ricinoleic acid has been esterified. However, other reactions can also take place. For example, the double bond can be attacked to produce an ester or the hydroxysulfonic acid (33). Hydrolysis of the sulfuric acid esters occurs during the reaction and subsequent treatment forming hydroxy acids and sulfuric acid. These hydroxy acids can be further sulfated.

Despite the many reactions and complex mixture obtained by the sulfuric acid treatment, most commercial products seem to be similar in properties (34). Commercially sulfated castor oil contains ca 8.0–8.5 wt % combined SO_3, indicating that the surfactant properties result from the sulfation of only one of the reactive points in the unmodified triglyceride. The sulfate group acts as a hydrophile imparting excellent wetting, emulsification, and dispersing characteristics to the oil. The anion-active product is used in the textile industry for fiber wetting ability and as dye agent to obtain bright, clear colors (35) (see Dyes and dye intermediates; Textiles).

Sulfonation of castor oil using anhydrous SO_3 yields a product having better hydrolytic stability than that from the sulfuric acid reaction. The organically combined SO_3 is low compared to the amount of SO_3 introduced to the reaction: the final product contains only 8.0–8.5 wt % combined SO_3 although 17 wt % SO_3 is added. The product contains less inorganic salts and free fatty acids than the sulfuric acid product (36).

4.3. Alkali Fusion

Tha alkali fusion of castor oil using sodium or potassium hydroxide in the presence of catalysts to split the ricinoleate molecule, results in two different products depending on reaction conditions (37, 38). At lower (180–200°C) reaction temperatures using one mole of alkali, methylhexyl ketone and 10-hydroxydecanoic acid are prepared. The 10-hydroxydecanoic acid is formed in good yield when either castor oil or methyl ricinoleate [141-24-2] is fused in the presence of a high boiling unhindered primary or secondary alcohol such as 1- or 2-octanol. An increase to two moles of alkali/mole ricinoleate and a temperature of 250–275°C produces capryl alcohol [123-96-6], $C_8H_{18}O$, and sebacic acid [111-20-6], $C_{10}H_{18}O_4$, (39–41). Sebacic acid is used in the manufacture of nylon-6,10.

4.4. Production of Nylon-11

Nylon-11, which accounts for the world's largest single use of castor oil, has unique stability and solvent-resistant properties. Its preparation is based on the steam cracking/pyrolysis of methyl ricinoleate (42) produced from the reaction of castor oil and methyl alcohol. Pyrolysis of methyl ricinoleate at ca 450–500°C yields methyl 10-undecylenate and heptaldehyde [111-71-7], $C_7H_{14}O$. Hydrolysis gives 10-undecylenic acid [112-38-9], $C_{11}H_{20}O_2$, which upon addition of HBr in the presence of peroxides forms 11-bromoundecanoic acid. This acid reacts with ammonia to form aminoundecanoic acid, known as rilsan monomer (43). Heating of the molten monomer gives the nylon-11 polymer (see Polyamides; Fibers, polyamides).

Nylon-11, mp of ca 186–190°C facilitating high speed uniform processing, has the advantage of having a cold impact, no rupture temperature of -40 to $-50°C$, low moisture sensitivity, and very high zinc chloride resistance. Excellent chemical resistance and stability in contact with all types of fuels, along with vibration and shock resistance, have led to the use of nylon-11 in the automotive industry, as a covering for braided cable, and in industrial fabrics. A variety of bearing and rollers in conveyor systems are fabricated from this material.

The use of nylon-11 for powder coatings or dry coatings (qv) has been developed in response to a growing concern for the environment (44) (see Coating processes, powder technology). Electrostatic deposition allows thin films to be applied to metal substrates. Once the powder is applied, it must be melted and coalesced into a continuous plastic film. Forced draft or irradiant ovens are used for fusion, and because no polymerization or cross-linkage are required for curing, coated objects can be processed quickly and air-cooled (45).

4.5. Hydrogenation

Hydrogenation of castor oil must be carried out at relatively low temperature and pressures to preserve the hydroxy group, functional in the preparation of 12-hydroxystearic acid [106-14-9], $C_{18}H_{36}O_3$, used for the manufacture of automotive and multipurpose greases (see Lubrication and lubricants). Optimal results are obtained at $130 \pm 5°C$ at a pressure of 1.5–2.0 MPa (15–20 bars) using 0.2 wt % nickel catalyst. Other catalysts and processing parameters may be used to produce unique derivatives. Simple double-bond hydrogenation at 140°C in the presence of Raney nickel catalyst produces glyceryl tris(12-hydroxystearate) [139-44-6], $C_{57}H_{110}O_9$, having a melting point of 86°C (46, 47).

Approximately 40,000–45,000 metric tons of hydrogenated castor oil and 12-hydroxystearic acid are produced annually, accounting for about 10% of the world castor oil production. The hydrogenated castor oil and 12-hydroxystearic acid are used primarily for the manufacture of lubricating greases in the form of lithium soaps. Petroleum-derived base stock containing approximately 8% lithium soap is used as an automotive grease. Special high viscosity greases contain 20–30% of the lithium 12-hydroxystearic soap. The needlelike structure of the soaps impart better stability and lubricity to greases that are impervious to water. They perform better than tallow stearate containing greases (48).

Conversion of castor oil or the methyl ester to the fatty alcohol can be accomplished by sodium reduction or high pressure hydrogenation. Quantitative reduction to ricinoleyl alcohol [540-11-4], $C_{18}H_{36}O_2$, is achieved using a secondary reducing alcohol in the presence of sodium suspensions in refluxing xylene. Hydrogenation of ricinoleic acid using a copper–cadmium catalyst at 220°C and 26 MPa yields 70% ricinoleyl alcohol (49).

The preparation of methyl 12-ketostearate from methyl ricinoleate has been accomplished using copper chromite catalyst. The ketostearate can also be prepared from methyl ricinoleate in a two-step process using Raney nickel. The first step is a rapid hydrogenation to methyl 12-hydroxystearate, the hydrogen coming from the catalyst, followed by a slower dehydrogenation to product (50, 51).

Partial hydrogenation of castor oil results in waxes (qv) of modified chemical properties when hardness, flexibility, melting point, and iodine value of the products are controlled by degree of hydrogenation. Castor oil esters are changed by hydrogenation from fluid products to soft waxes having mp of 45–80°C. These products are used in antiperspirants (see Cosmetics), leather (qv) coatings requiring oil resistance and water imperviousness, and in roll leaf foils because of their alcohol solubility and excellent wetting adhesion to metallic particles.

4.6. Pyrolytic Decomposition

The pyrolytic decomposition at 350–460°C of castor oil or the methyl ester of ricinoleic acid splits the ricinoleate molecule at the hydroxyl group forming heptaldehyde and undecylenic acids. Heptaldehyde, used in the manufacture of synthetic flavors and fragrances (see Flavors and spices; Perfumes) may also be converted to heptanoic acid by various oxidation techniques and to heptyl alcohol by catalytic hydrogenation. When heptaldehyde reacts with benzaldehyde, amyl cinnamic aldehyde is produced (see Cinnamic acid, cinnamaldehyde, and cinnamyl alcohol). Undecylenic acid, the nylon-11 precursor, is also used for its fungicidal and bactericidal properties. A combination of undecylenic acid and zinc undecylenate [557-08-4] is used in the treatment of athlete's foot infections. The copper salt has been compounded into ointments used in treating facial and body infections (52) (see Antiparasitic agents).

4.7. Alkoxylation

Alkylene oxides react with the hydroxyl groups of castor oil to yield an infinite variety of polyoxyalkylene derivatives. The reaction at 120–180°C and 0–415 kPa (0–60 psi) uses alkaline catalysts such as sodium hydroxide. Free-radical-type acid catalysts are also used at lower temperature and pressure (53). The most important group of products, the ethoxylated derivatives, are nonionic surface-active agents having various degrees of hydrophobic/hydrophilic properties. The low level ethyoxylated derivatives are water emulsifiable and used as defoamers (qv) and de-emulsifiers for petroleum emulsions. The highly ethoxylated products are water-soluble and excellent solubilizers for water-insoluble oils in cosmetic compositions (54–56). They are also used as components in detergents, lubricating and cutting oils, hydraulic fluids (qv) (57), textile finishing compositions, and as antistatic agents (qv) for nylon carpets and apparel (58, 59). The propoxylated derivatives are mineral oil-soluble and useful in lubricating oils and hydraulic fluid compositions. Approximately 6500 metric tons of ethoxylated castor oil were produced in the United States in 1988.

4.8. Oxidation

Oxidized or blown castor oils are clear viscous oils that are made by the intimate mixing (blowing) of castor oil and air or oxygen at 80–130°C, with or without the use of a catalyst. The reaction is a combination of oxidation and polymerization promoted by transitionary metals like iron, copper, and manganese (60, 61). The range of the properties of commercially available oils are given in Table 8.

Table 8. Properties of Oxidized Castor Oils

Property	Value
color (Gardner)[a]	2–13
viscosity at 25°C, $mm^2/s(=cSt)$	1,100–200,000
specific gravity at 25°C	0.970–1.028
acid value	5–25
saponification value	188–225
iodine value	80–50
hydroxyl value	160–125

[a] Color ranges from pale to dark brown.

Table 9. World Production and Trade of Castor Oil, t/yr (1986–1989)

Country	Production[a]	Exports[b]	Imports[b]
Brazil	100,350	79,852	
India	85,750	39,667	
China	65,341	26,495	
Russia[c]	26,525		357,000
Germany[d]	17,000	5,430	10,988
Japan	15,416	181	
Thailand	15,313	8,950	
United States			36,850
France			41,781
United Kingdom			8,420
Poland			4,695
The Netherlands			3,776
Total	*359,839*	*167,558*	*167,972*

[a] Ref. 63.
[b] Ref. 64.
[c] Figures are for the former USSR.
[d] Figures are for the former FDR (West Germany).

Oxidized castor oils are excellent nonmigrating, nonvolatile plasticizers (qv) for cellulosic resins, poly(vinyl butyral), polyamides, shellac, and natural and synthetic rubber (see Rubber, natural). The high viscosity products are also used as tackifiers in gasket compounds and adhesives (qv) because of good oil and solvent resistance. They also serve as excellent pigment grinding media and as a base for inks (qv), lubricating oils, and hydraulic oils (62).

5. Economic Aspects

Whereas castor oil is available on a worldwide basis from many sources, India, Brazil, and China produced nearly 80% of the world's castor seed for the period 1986–1989 (63) as seen in Table 9. In the small number of significant producing and exporting nations that grow castor, traditional agricultural practices are used, and practically all castor plants are grown under dryland conditions and hand harvested. Much of the castor crop is harvested from small farms that are fully dependent on natural weather conditions, contributing to fluctuations in both supply and price. Yield of castor seed per acre is reported at 270–450 kilograms per acre.

Wholesale prices for No. 1 castor oil in tank car lots was \$1.11/kg in 1990 compared to \$1.60/kg in 1984 and \$0.74/kg in 1986 (65). Brazil, China, and India accounted for about 85% of the world exports, and France, the United States, Russia, Germany, and the United Kingdom accounted for about 75% of the world imports from 1986–1989.

A more reliable castor oil supply is being sought through genetic efforts. In 1985, a project was established in Costa Rica for the production of hybrid castor seeds to improve the oil content of the seed, make the seed totally nondehiscent, ie, prevent the seed from breaking out of the capsule and falling to the ground as it ripens allowing for mechanical harvesting (66). The European Community (EC) lists castor production as the number one demonstration priority, and the Costa Rican technology has been utilized in France where hybrid castor seed for mechanical harvesting was planted in 1990. A project was also initiated in the United States in 1989 to revive domestic production of castor seed on the high plains of Texas (67). A hybrid castor seed (H-22), developed by the Weizman Institute in Israel, is most widely used by underdeveloped countries where crops are hand harvested. New dwarf varieties are being developed for mechanical harvesting (68).

6. Applications

Castor is the only renewable vegetable oil resource (see Chemurgy) having a hydroxyl group structure and functionality that leads to diverse oleochemicals. In 1988, approximately 35,000 t/yr of castor oil were used to prepare raw materials for the manufacture of nylon-11. It is estimated that 40,000–45,000 t of oil are used annually to manufacture hydrogenated castor oil waxes and 12-hydroxystearic acid for automotive greases. In 1989, the United States used 15,000 t of castor oil to manufacture sebacic acid and ethoxylated castor oils, and India used 35,000 t of oil for the manufacture of raw materials used in surface coatings (69).

6.1. Polyamides

Nylon-11, accounts for the largest single use of castor oil. Pyrolysis of the oil yields methyl undecylenate, which is converted to 11-amino-undecanoic acid. Condensation of this monomer produces nylon-11, known commercially as Rilsan 11 (Atochem, Inc.). Nylon-11 is used as an engineering plastic in the automotive and transport industry in the form of fuel lines. Products are also used for extruded and molded components of fuel systems such as filler necks, gas tanks, reservoir modules, filters, fuel rails, and vapor recovery systems. Air brake hoses on large trailer truck transports are made of nylon-11, and nylon-11 tubing is used in the compressed air industry in pneumatic control systems. In addition, nylon-11 is used in powder coatings to coat metals that require abrasion, impact, and corrosion resistance. Nylon-11 offers high dimensional stability, close molding tolerance, high abrasion and impact resistance, excellent dielectric strength, low moisture absorption, electrical insulating properties, and overall chemical resistance and durability (45, 70).

6.2. Urethanes

Castor oil is used as a reactive component with polyfunctional isocyanates to prepare polyurethane compounds (see Urethane polymers). Castor oil has been polymerized with toluene diisocyanate (see Isocyanates, organic) and combined with polystyrene phase to produce a semi-interpenetrating polymer network upon heating. This interpenetrating polymer network provides a route for improving brittleness of thermosetting plastics and increasing the morphology and toughness of the final elastomer. Tough plastics were derived based on castor oil-elastomer-reinforced vinyl polymers (qv) and simultaneous interpenetrating networks prepared by cross-linking castor oil with sebacyl chloride and polystyrene (see Styrene plastics) (71–73). Water-resistant polyurethane-based encapsulants were prepared from castor oil polyols and plasticizers. The cured elastomer is used to encapsulate plastic insulated telephone cables and seal the interior spaces of the electrical connections from the incursion of water (74–77).

Urethane casting resins prepared from castor polyols exhibit a broad range of properties from hard plastics to soft elastomers. These two-component liquid urethanes are reported to have good electrical and mechanical properties, good shock absorption, low exotherm, low shrinkage, and excellent hydrolytic stability and heat aging properties (78–81). These castor-based casting resins are used principally for potting and encapsulation of electrical components.

Low viscosity urethane polymers have been prepared from castor oil and polymeric isocyanates (82). These low mix viscosity systems are extremely useful for potting electrical components where fast penetration without air voids, and fast dispensing cycles are desirable. Very low viscosity urethane systems containing castor polyols have been prepared for use in reclaiming water-logged buried telephone cable and for encapsulating telephone cable splices (83–86).

Polymerization of castor oil, chemical or oxidative, results in higher viscosity or bodied oils that are more useful in urethane coatings than the untreated castor oil (87). Other castor derivatives used to prepare urethanes are amides prepared by reaction of castor oil and alkanolamines, amides of ricinoleic acid with long-chain di- and triamines, and butanediol diricinoleate (88, 89).

By varying molecular weight and functionality of the castor polyols and the type of isocyanate, a variety of clear and pigmented urethane coatings can be prepared. Copolymers of vinyl and castor-based urethane have also been reported for use as exterior coatings for plywood and flexible substrates (90) and for application over steel, concrete, and wood substrates (91).

Castor oil and its polyol derivatives have been found to be very useful in the preparation of rigid, semirigid, and flexible urethane foams. Castor oil's resistance to hydrolysis, pigment dispersion ability, and compatibility with polyether polyols has also made it useful as a modifier for polyether-based foam. These foams generally possess an open cell structure (92). Castor oil can also be used to formulate commercially acceptable rigid urethane forms for such uses as thermal insulations and structural support (93). Superior rigid urethane foams have been prepared from hydroxymethylated polyol esters of castor acids (94). Brominated castor oil has been investigated as a modifier for preparing fire-resistant urethane foams (95, 96).

6.3. Coatings

A variety of castor oil derivatives are utilized in the preparation of surface coatings (qv). Dehydrated castor oil fatty acids (DCOFA) react with phthalic anhydride and other polyols to produce a water-soluble, air-drying alkyd resin (97). Reaction of an acrylamide polymer, combined with styrenated acrylates and an oil modified maleic polyester, is effective in producing appearance finishes, and aluminum coil and metal protective coatings (98). Copolymerization of DCOFA with acrylic esters or reaction of DCOFA with hexamethoxy methylolated melamine resins followed by neutralization with ethyl amine give an aqueous solution useful as a water-soluble resin for an electrodeposition coating (99). Aliphatic polyurethane coating compositions are prepared from trimethylolpropane, dehydrated castor oil fatty acids, 4,4-dicyclohexylmethane diisocyanate, and other components to prepare a weather-resistant finish suitable for use on motor vehicles (100). Coatings from castor oil—toluene diisocyanate copolymers exhibited high abrasion resistance on steel plates and flexibility on aluminum plates and PVC cloth.

A copolymer latex emulsion system utilizing dehydrated castor oil fatty acids yields superior wall paints providing adhesion to varnishes and glossy surfaces (101). Acrylic esters of castor oil are used in solution for the emulsion polymerization coatings process. Water-soluble resins and paints prepared with maleated dehydrated castor oil were used in electrodeposition of water-soluble primers containing 10 to 15% solids for optimum paint film thickness (102). Cathodically electro-depositable binders prepared using dehydrated and maleated dehydrated castor oil fatty acids resulted in binders that gave good adhesion of maximum film thickness (103–105).

6.4. Lubricants

Selection of lubricants is based on ability to mitigate wear and friction under the overall conditions of the intended application. Lithium 12-hydroxystearate gives superior thickening and grease forming properties because of the hydroxyl group and helical structure of its crystalline form (106). Sebacic acid, produced by the alkali fusion of castor oil, is the raw material for a series of esters used as nonvolatile, high temperature lubricants for jet engines (107, 108). Partially dehydrated castor oils and USP grades of castor oil are approved for trolley lubrication in meat packing plants and extended to applications for lubricants having incidental food contact (109, 110).

Sulfated castor oil is incorporated with mineral oil and isopropylamine salts of C_{12}–C_{18} fatty acids as a lubricant for presizing polyester fibers. The lubricant minimized undesirable abrasion of sizes and facilitated subsequent weaving operations (111). A nontoxic lubricating cutting oil for metals at 700–1200°C is prepared from aluminum powder, graphite, potassium soap, and castor oil (112).

6.5. Textiles

Polyamides having improved antistatic properties utilize polyoxyalkylated hydrogenated castor oil as the dispersible antistatic agent (113). A finish for bulked continuous polyamide filament yarns also use polyoxyethylated castor oil to enhance the fiber finish (114).

Different polyamide fibers with varying affinities for anionic dyes are pretreated with aqueous acidic solution containing sulfated castor oil to give uniform shade levels. Sulfated castor oil is also used in compositions for treatment of fabrics, skins, and furs to clean and revive colors (115).

6.6. Cosmetics

Castor oil and its derivatives are utilized in cosmetic and personal care products. The low pour point and high viscosity produce lubricity and wetting properties desired in lipsticks. Basic lipstick contains 20–44 wt % castor oil, which also acts as an ideal dispersant for pigments (116). One lipstick formula contains 38 wt % castor oil and 9.5% glycerol monoricinoleate (117).

Castor esters have been found to be nonirritating and noncomedogenic to the skin. Cetyl ricinoleate was found to be an effective noncomedogenic moisturizer (118). Castor-based quaternaries prepared by reaction of a castor fatty acid and a tertiary diamine are used for hair care. The ricinoleic quaternium is incorporated into clear shampoo formulations for foam enhancement and conditioning (119, 120).

Hydrogenated castor oils are utilized as a principal ingredient in the manufacture of solid antiperspirant stick formulations. The high melting point of the wax reduces the solidification time in the manufacture of the sticks, resulting in a uniform dispersion of the antiperspirant active ingredients. Hydrogenated castor oils impart emollient and lubricant properties to ointment and cosmetic preparations and act as thixotropic agents in cosmetic gels (118).

Ethoxylated castor oils or ethoxylated castorwaxes are used as solubilizers of hydrophobic substances in cosmetics. Examples are Cremophor EL (ethyoxylated castor oil) and Cremophor RH (40/60 ethoxylated hydrogenated castor oil). Other ethoxylated triglycerides are not as effective as castor oil. Ethoxylated castor oil is also a good solubilizer for vitamin A palmitate (121).

6.7. Surfactants and Dispersants

Castor oil can be transformed from an oil- to a water-soluble surfactant, depending on the moles of ethylene oxide added to its hydroxyl group. A 40 mole ethylene oxide adduct of castor oil, known as PEG-40 castor oil, is a surfactant that has cosolvent properties and is utilized as a fragrance solubilizer (118). Glycol hydroxystearate emulsifiers are formulated into shampoos to impart finer pearlescence and give better stability than gylcol stearates (118) (see Hair preparation).

Castor oil fatty acid amide polyethylene ethers exhibited dispersant, antimicrobial, emulsifying, and wetting properties. Combining the ethers with magnesium ricinoleate exhibited rust inhibition on aluminum, iron, and brass (122).

Mixtures containing sulfated castor oil were used to increase the lubricity of water base drilling fluids (123). Sulfated castor oil is also used in dishwashing compounds as a hand softener. A typical cleaning composition contains sodium dodecylbenzene sulfonate, sulfated castor oil, ethanol, and water. A sulfated derivative of castor oil is used as a dispersant for plaster of Paris, reducing the water needed to form a plastic slurry (124). Pesticide emulsions can be stabilized using ethoxylated castor oil (125).

Using sulfated castor oil in the electroplating of zinc results in a good coating, a brilliant plate, and fairly good covering (126). Emulsified noncreosotic pine oil disinfectant compositions have been prepared using <7 wt% of an emulsifier mixture and soaps of castor oil and mixture of soaps of tall oil(127), and a red stamp ink composition, by dispersing pigment particles coated with ethyl cellulose in alkylene oxide modified castor oil (128). A partially saponified castor oil, prepared by reaction of an ethoxylated castor oil and alkali metal hydroxide, resulted in surfactants of excellent detergency, low foaming characteristics, stability in alkali and acid solutions, complete water solubility, and no cloud point in typical aqueous use solutions (129).

Polyoxyethylated castor oil containing 42 moles of ethylene oxide may be used under the Federal Food, Drug, and Cosmetic Act as an emulsifier in nitrocellulose coatings for paper and paperboard intended for use in contact with fatty foods at a maximum level of 8 wt % of the coating solid (130).

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