THE NEWEST MIRACLE INGREDIENT REDISCOVERED

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The cosmetic chemist has long been in search of ingredients that provide topical benefits to the skin, including gloss, decreasing transepidermal water loss (TEWL), lubrication, conditioning and emoliency. In addition, if one includes in the search for products useful in wetting pigments and that are formulator friendly providing benefits like being water dispersible or self-emulsifying, the search, using classical chemistries, the chance of success becomes almost impossible.

What if a product that has been around for a thousand years were given a different chemical "twist" and provided all of the above? Surely it would be called "A MIRACLE INGREDIENT "Just as aspirin has been rediscovered so has castor oil. The "twist" so to speak is the polymerization and functionalization of castor oil.

Castor oil ? Yes castor oil ! Let us review what it is that we know, dislike and love about this ancient product

We know that Castor oil is a unique triglyceride[1]. It is derived from Ricinus communis L. The castor plant grows wild in many subtropical and tropical areas. Today Brazil, China and India provide over 90% of the oil. Castor Oil is a clear, viscous, light colored fluid that is nondrying and quite stable. The Purity of Castor Oil (89%)occurs with remarkable uniformity. Regardless of country of origin, or season it is grown, the composition and chemical properties remain within a very narrow range. Castor Oil has broad compatibility with oils, waxes, natural resins, and gums.

Castor Oil *(Ricinus communis)*[2]

Source

Castor oil is a unique triglyceride. It is derived from Ricinus communis L. The castor plant grows wild in many subtropical and tropical areas. Today Brazil, China and India provide over 90% of the oil. Castor oil contains a large content of hydroxy containing compounds that are unsaturated.

This versatile material is a clear, viscous, light colored, freely flowing fluid that is nondrying and quite stable. The purity of composition of Castor Oil occurs with remarkable uniformity. Regardless of country of origin, or season it is grown, the composition and chemical properties remain within a very narrow range. Castor Oil has broad compatibility with oils, waxes, natural resins, and gums.

B. Carbon Distribution

Component	Typical % Weight
C16:0	1
C18:0	1
C18:1-OH	89
C18:1	3
C18:2	6

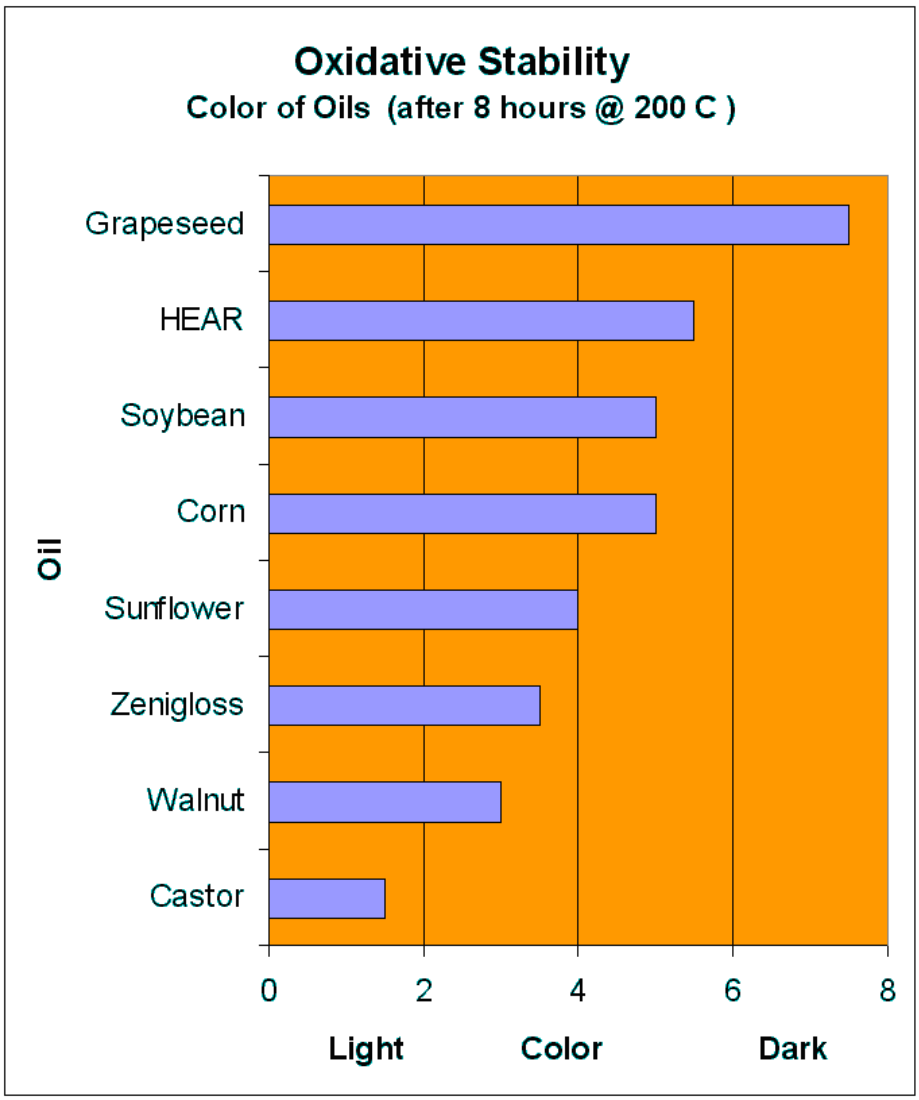
CAS Number: 8001-79-4

EINECS Number: 232-293-8

Titer Point 2 ° C

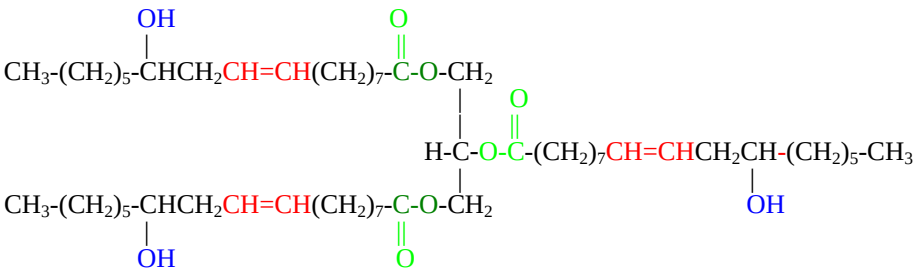
Iodine Value: 85

Castor oil is a high purity oil in terms of carbon chain distribution as provided by nature! This makes Castor oil both compositionally pure and natural. Castor oil also has outstanding oxidative stability, in spite of its unsaturation. We can demonstrate this by looking at color formation at 200^{o} C. Refined oils were held at this temperature and color change monitored [3]. The results are in graphic 1.



Chemical Structure

The chemical structure of castor oil shows why it is so important to making a suitable polymer. The structure is:



The OH is a hydroxyl group, the CH=CH is an alkene and the C(=O)-O is an ester.

The castor polyesters of interest use the three-hydroxyl groups to make the polymer and to incorporate functional groups onto the polymer.

Many polymeric materials are made by the free radical polymerization of vinyl containing monomers to form high molecular weight polymers. These polymers of times have desirable properties, but also contain residual unreacted monomer. This residual monomer is undesirable.

The approach to making products of this type has forced chemists to look at new raw materials, processes and reaction parameters in an attempt to make a suitable cosmetically acceptable product. This approach continues, but another approach that has worked is not based upon the polymerization of vinyl containing monomers. This means the products contain no free vinyl monomers! The polymers are based upon the naturally occurring products castor oil and succinic acid. The polymers can be made to varying

molecular weights, allowing for the custom selection of viscosity, playtime on the skin and penetration of the skin. Finally, by placing functional groups on the polymer, a variety of properties like gloss, conditioning, and hardness can be effected.

Polyesters

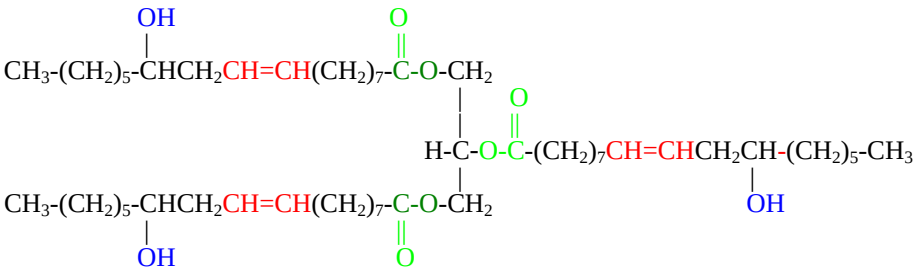
The castor polymers of interest are polyesters. That is polymers that contain a number of castor oil groups linked together through a ester bond. In order to make polymers, there must be at least two raw materials that contain multiple reactive groups[4]. In this case the poly hydroxyl group is provided by castor oil and the poly acid is succinic acid

Castor Succinate Polyester – The Backbone for Functional Polymers

The reaction of castor, with its three-hydroxyl groups with succinic acid and its two-hydroxyl groups is the first step in the creation of the polyester. Figure 1 shows the reaction. The first step is reaction of one carboxyl group with one hydroxyl group.

Polyester Reaction

Figure 1



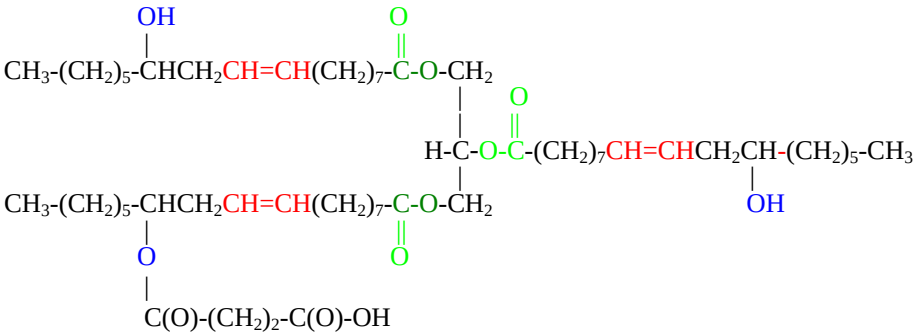
Castor oil

(a tri-hydroxy compound)

+ $HO\text{-}C(O)\text{-}(CH_2)_2\text{-}C(O)\text{-}OH$ ----------→

Succinic acid
(a dicarboxylic acid)

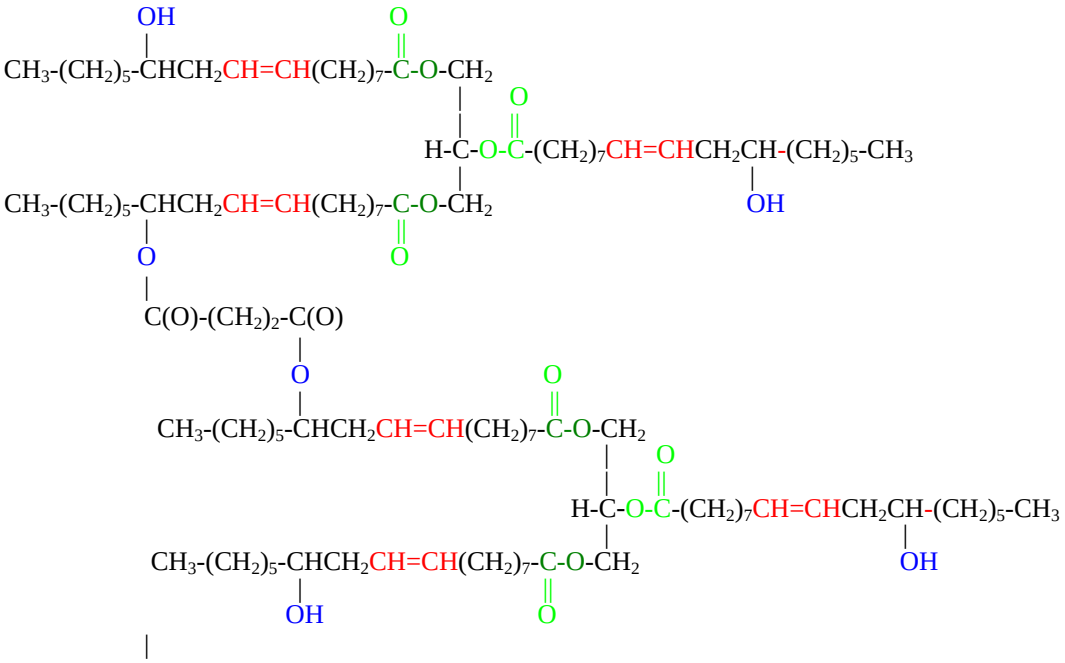
$-H_2O$



Castor succinate di-ester

It should now be clear why there is no free vinyl monomer in the product. There is simply none used in the reaction. The monomers are castor oil and succinic acid. This carboxylated castor oil still has a free carboxylic group, which reacts in turn with another hydroxyl group on another castor oil to make a diester as shown in figure 2.

Figure 2
Diester

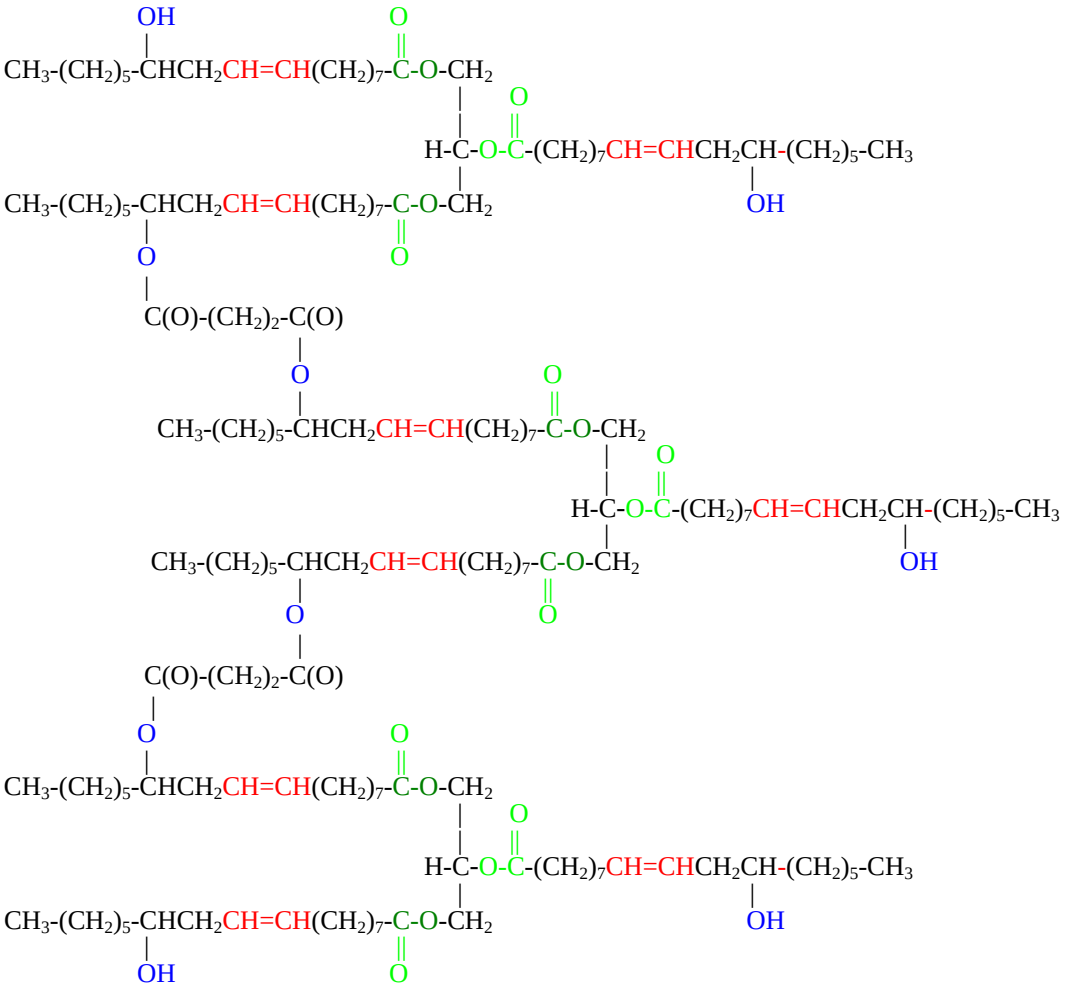


Castor Succinate diester

If only one succinic acid is added per castor, given the correct catalyst and process conditions, the above product results. The diester product has no free acid groups and four free hydroxyl groups. The degree of polymerization (so called “dp”) is 2. The molecular weight of the material has more than doubled and the polarity decreased compared to castor oil.

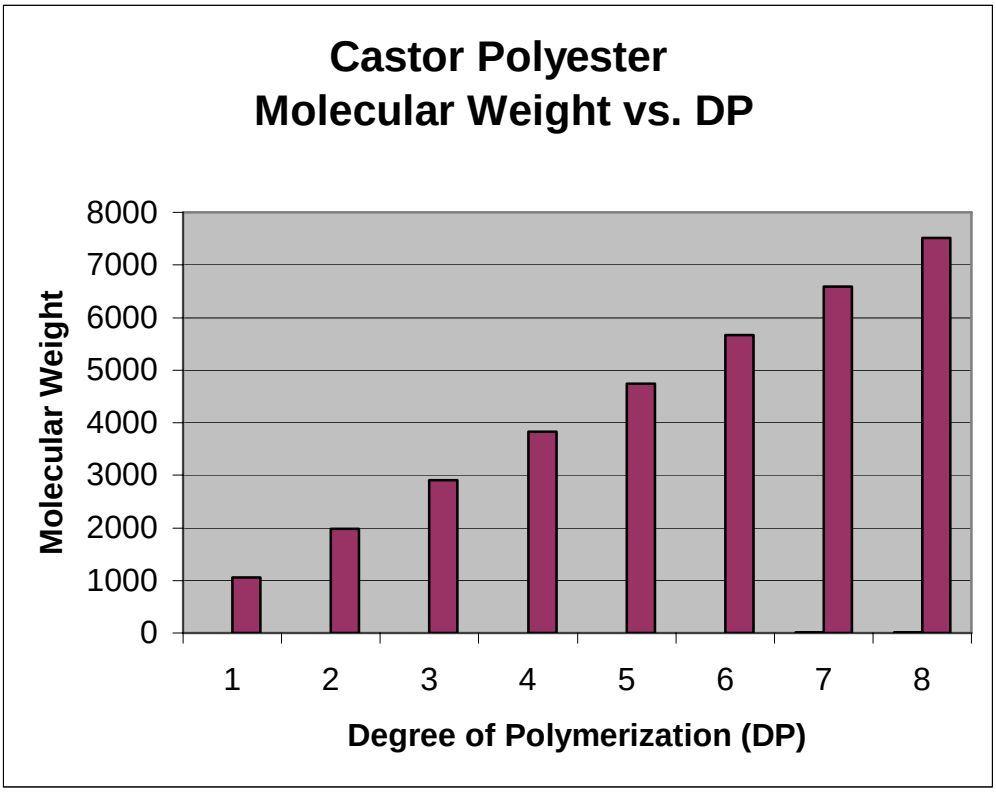
If one continues to add succinic acid, the polymer will grow, that is the dp will increase.

Figure 3
Polyester



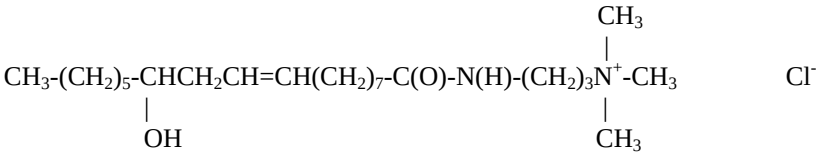
Castor Succinate polyester (dp =3)

The lowest molecular weight polyester has a dp of 3, has three castor oils linked together, and has 5 remaining hydroxyl groups, having started with nine. As one continues to increase the amount of succinic relative to castor, the “dp” increases and more of the center castor groups are added.



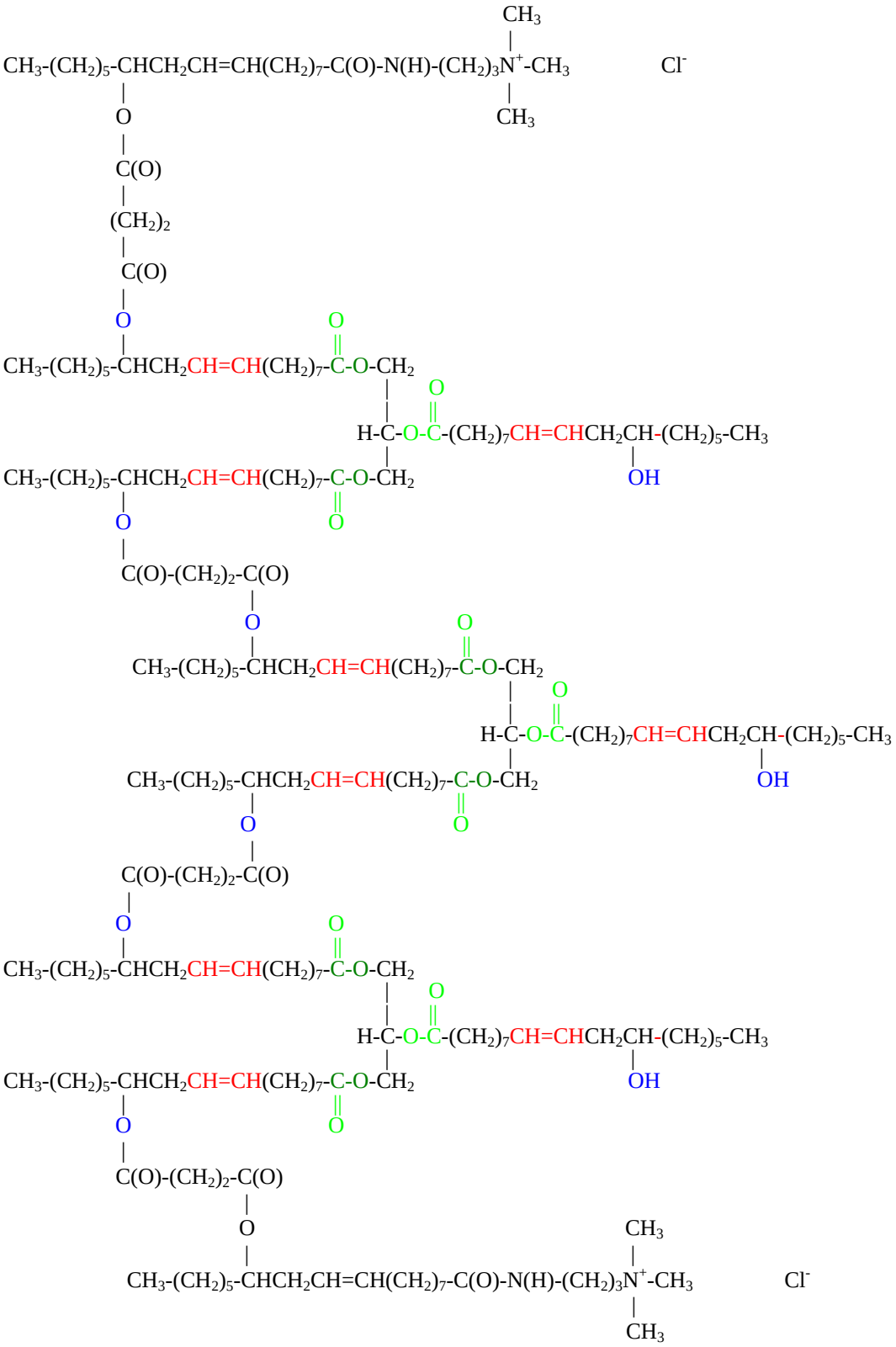
Polymer Capping

The introduction of a mono-hydroxy compound into the reaction mixture will result in a capping of the molecule, and an introduction of functionality. One such capping group is ricinoleylamidopropyl trimethyl ammonium chloride.



If the proper ratio and reaction conditions are employed the following simple polyester is made:

Cationic Polyester
Figure 3



The resulting polymer is cationic (with two cationic sites) and thus provides substantive conditioning and gloss to hair.

Functionalization of the Backbone

If the free hydroxyl groups on the polyester are esterified with fatty acid, a glossing compound results. The exact properties of the compound, like gloss, playtime and viscosity are determined by the "dp" (degree of polymerization) of the particular polyester. The higher the "dp" of the polyester, the higher the molecular weight, the viscosity, the playtime and the lower the penetration. If the acid used to cap is saturated and has 18 or more carbon atoms, a solid polyester will result. The specific fatty acid chosen will determine the melting point and hardness of the polyester.

Castor Succinate Polyester

FEATURE	BENEFIT
1. 100% active	**1. High total performance product. Fully functional.**
2. Pigment wetter.	**2. Improves color brightness.**
3. Versatile.	**3. Hair, skin, sun and color applications.**
4. Natural organic ingredients.	**4. No petroleum base or phenyl groups. Biodegradable**
5. High molecular weight .	**5. Gives high substantivity and gloss. Little penetration of the skin.**
6. High oxidative solubility.	**6. Retards dicoloration in finished formula.**
7. Known ingredient (castor oil and succinic acid).	**7. Easy to formulate product.**

USES / APPLICATIONS

Shampoos	Eyeliner pencils	Conditioner
2-in-1 Shampoos	Leave-in conditioner	Lip-gloss stick
Lipsticks	Liquid makeup remover	Lip-gloss pots
Makeup pencils	Makeup remover spray	Sun tan oils
Hair gloss sprays	Hair pomades	Hair colorant with shine

Formulations

The following formulations demonstrate the use of the various castor succinate polyester compounds.

SHEEN SPRAY WITH GLOSS

LAB # CLI: 12109/1

NO.	PHASE	INGREDIENT	% BY WEIGHT
1.	A	Diethylhexyl Sebacate	38.0
2.	A	Cyclomethicone	40.0
3.	A	Octyl Methoxycinnamate	1.0
4.	A	Melaleuca Alternifolia (Tea Tree) Leaf Oil	0.2
5.	B	Castor Isostearate Succinate **(CASTOR POLYMER)**	20.0
6.	B	Tocopheryl Acetate	0.1
7.	B	Retinyl Palmitate	0.1
8.	B	Ascorbyl Palmitate	0.1
9.	B	Fragrance	0.5
		Total	100.0

Manufacturing instructions:

Combine Phases A and B at room temperature. Add Phase B to Phase A. Package.

HAIR CONDITIONER WITH GLOSS

LAB # CLI: 12102/2

NO.	PHASE	INGREDIENT	% BY WEIGHT
1.	A	Water	83.5
2.	A	Glycereth-26	2.0
3.	A	Dicetylmonium Chloride	2.0
4.	B	Peg-40 Stearate	0.5
5.	B	Cyclomethicone	5.0
6.	B	Cetearyl Alcohol	2.0
7.	B	Cetearyl Alcohol (and) Ceteareth-20	2.0
8.	B	Ricinoleic Succinic Polyester (Pending) **CASTOR POLYMER**	3.0
9.	B	Behentrimonium Methosulfate (and) Cetearyl Alcohol	3.0
10.	C	Fragrance	0.4
11.	C	DMDM Hydantoin	0.2
12.	D	Sodium Hydroxide	As Required
		Total	100.0

Manufacturing instructions:

1. Heat Phase A to 75^{o}C. Heat Phase B to 75^{o}C.
2. Add Phases B to Phase A while maintaining temperature 70 – 75C.
3. Cool to 40C and add Phase C.
4. Adjust pH to 5.0.

Lip Gloss Stick

ANH4-15-1

INCI Name	**%**
Castor Oil	28.7
Carnauba	2.0
Candelilla	7.5
Ceresin	3.5
Triisostearin	20.0
Octyldodecanol	6.0
CASTOR ISOSTEARATE SUCCINATE BEESWAXATE (CASTOR POLYMER SOLID)	25.0
Polyglyceryl-3 Diisostearate	5.0
Silica Dimethyl Silylate/Castor Oil	2.0
Methyl paraben	0.2
Propyl paraben	0.1
	100.0

Manufacturing instructions:

1. Prewet the Silica Dimethyl Silylate/Castor Oil in the castor oil.
2. Mill until homogenous using a three roll mill.
3. Combine all ingredients.
4. Heat to 85 – 90^{o}C with stirring until clear.
5. Stir and allow to cool down to 70 – 72^{o}C and fill.

HAIR CONDITIONER WITH GLOSS

LAB # CLI: 12102/2

NO.	PHASE	INGREDIENT	% BY WEIGHT
1.	A	Water	83.5
2.	A	Glycereth-26	2.0
3.	A	Dicetylmonium Chloride	2.0
4.	B	Peg-40 Stearate	0.5
5.	B	Cyclomethicone	5.0
6.	B	Cetearyl Alcohol	2.0
7.	B	Cetearyl Alcohol (and) Ceteareth-20	2.0
8.	B	Castor Isostearate Succinate **Castor Polymer**	3.0
9.	B	Behentrimonium Methosulfate (and) Cetearyl Alcohol	3.0
10.	C	Fragrance	0.4
11.	C	DMDM Hydantoin	0.2
12.	D	Sodium Hydroxide	As Required
		Total	100.00

Manufacturing instructions:
1. Heat Phase A to 75C.
2. Heat Phase B to 75C.
3. Add Phases B to Phase A while maintaining temperature 70 – 75C.
4. Cool to 40C and add Phase C.
5. Adjust pH to 5.0.

LOTION CONDITIONER for DAMAGED HAIR

NO.	PHASE	INGREDIENT	% BY WEIGHT
1.	A	DEIONIZED WATER	89.35
2.	A	GUAR HYDROXYPROPYL TRIMONIUM CHLORIDE	0.20
3.	A	SILICONE PANTHENOL QUAT	0.30
4.	B	CETEARYL ALCOHOL	2.00
5.	B	PEG-40 STEARATE	0.25
6.	B	BEHENAMIDO TRIMETHYL AMMONIUM CHLORIDE	2.00
7.	B	Castor Isostearate Succinate and Ricinoleamidopropyl trimonium chloride **CASTOR POLYESTER QUAT**	3.00
8.	C	KATHON CG	0.05
9.	D	FRAGRANCE (HERBAL TYPE)	0.15
10.	E	NaOH (20% SOLN) QS TO PH 4-5	As Required
		Total	100.0

Manufacturing instructions:

1. Heat Phase A to 75^{o}C.
2. Heat Phase B to 75^{o}C.
3. Add Phases B to Phase A.
4. Cool to 45^{o}C and add remaining Phases.

SUNSCREEN EMULSION

NO.	PHASE	INGREDIENT	% By Weight
1	A	Water	53.65
2	A	Na_2EDTA	0.10
3	A	Propylene glycol	2.50
4	A	Keltrol T (2% soln)	15.00
5	B	Octyl methoxy cinnamate	7.50
6	B	Oxybenzone	3.00
7	B	Cetearyl alcohol	2.00
8	B	Octyl salicylate	5.00
9	B	Octyldodecanol	5.00
10	B	Cyclomethicone	2.00
11	**B**	Castor Isostearate Succinate and PEG ricinoleate **CASTOR POLYMER SELF EMULSIFYING**	3.00
12	B	Vitamin E acetate	0.25
13	C	Germaben II	1.00
		Total	100.00

Manufacturing instructions:
1.Combine Phase A at 75^{o}C.
2. Combine Phase B at 75^{o}C.
3. Add Phase B to Phase A.
4. Cool to 40^{o}C and add Phase C.

SOLID LIP GLOSS

INGREDIENT	**%**
Castor Oil	30.25
Carnauba	0.80
Candeliila	4.00
Ceresin (m.p. 75^{o}C)	1.60
Triisostearate	9.00
Castor Isostearate Succinate beeswax (Solid Castor Polymer)	25.00
Octyl Hydroxystearate	10.00
Octyldodecanol, Quaternium-18 Hectorite, and Propylene Carbonate (Bentone EUG)	6.00
Methyl paraben	0.20
Propyl paraben	0.10
COLOR GRINDS:	
35% CI 15820 (Red 7 Lake)/Castor Oil	0.55
25% CI 17200 (Red 33 Lake)/Castor Oil	1.30
40% CI 77491 (Iron Oxides)/Castor Oil	0.80
20% CI 42090 (Blue 1 Lake)/Castor Oil	0.40
Mica and Titanium Dioxide (Flamenco Red)	10.00
	100.00

ANH4-171

Procedure:

1. Prepare Color Grinds in advance using a three roll mill.
2. Combine all ingredients.
3. Heat to 85^{o}C with stirring until homogenous.
4. Cool with stirring to 58^{o}C and fill pans or jars.

The above formulations are believed to be accurate and is offered in good faith for the benefit of the customer. Zenitech however cannot assume any liability or risk involved in the use of its products since the conditions are beyond our control. Statements concerning the possible use of our products are not intended as recommendations for the infringement of any patent. These products are for commercial use only.

References

1. Karleskind, A. (Editor)**, Oils and Fats Manual,** 1996 Intercept Ltd, p 212.

2. O'Lenick, Anthony J., Steinberg, David and Klein, Kenneth, *Primary Ingredients*, 1998, available for download on www.zenitech.com.

3. Z**e**nitech Technical Bulletin 2001-5. p. 4

4. O'Lenick, Anthony J., **Surfactants Chemistry and Properties**, Allured publishing 1999, p. 77.