Vulcanized Meadowfoam Oil[1]

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The factice gelation time for meadowfoam oil, along with hardness, color, acetone extract and free sulfur content of the gelled products were compared with gelation time and product properties of factice prepared from seed oils of rapeseed, crambe, soybean, castor, *Lesquerella* and jojoba. The effect of additives, specifically zinc oxide, magnesium oxide, triethylamine, dicyclohexylamine, 2-mercaptobenzothiazole and iodine, was also investigated. Both white and brown factices could be prepared from meadowfoam oil and their properties were equivalent to or better than those from high erucic acid rapeseed oil used commercially for the highest quality factice.

KEY WORDS: **Brown factice, factice, *Limnanthes alba*, meadowfoam oil, vulcanization, vulcanized vegetable oil, white factice.**

Vulcanized vegetable oil, also known as factice, is used in rubber compounding to improve the quality of the product and reduce manufacturing costs. Factices give dimensional stability to extruded articles, reduce mold fill time and cure cycle time, improve the ozone resistance of the rubber compound, give a smooth velvety feel to rubber articles, reduce migration of oils and plasticizers to the surface of low durometer stocks, absorb a large amount of mineral oil and liquid plasticizers on the mill and in the Banbury mixer, and have the ability to flow or promote flow under mechanical pressure (1).

It has become customary to judge the quality of a factice by its physical properties such as color, hardness, acetone extract and free sulfur values. Free sulfur consists of unreacted or lightly bound sulfur. During the vulcanization of rubber, alongside the calculated amount of sulfur, free sulfur coming from factice will also participate in the crosslinking of the double bonds. This can lead to overcuring of rubber. Therefore industrially acceptable levels of free sulfur in factice do not exceed 2%. Acetone extract values show the amount of unsaponifiable oils, unreacted sulfur, and partially sulfurized glyceride oils that can be extracted from the polymer matrix. Acetone extract values not greater than 20% are considered first grade, greater than 20% of the weight of factice but less than 35%, medium grade, and greater than 35% commercial grade. However, a high acetone extract value does not necessarily imply that the factice is inferior for a particular application. In fact, factice is specifiable only by its actual performance in tests in rubber, and not by simple chemical tests alone (1).

Factice has been in use for more than a hundred years but only a limited number of vegetable oils are used in its preparation. The main factor in the choice of the oil is its cost. Unfortunately, most of the oils that are used for economical reasons, such as soybean oil and castor oil, take a longer time to gel than more expensive oils, are stickier and often more difficult to handle, and sometimes require additives or higher amounts of sulfur to improve the physical characteristics of the factice. There is a steady worldwide increase in the demand for rubber products and better quality rubber additives (2). With the favorable change in the market, the search continues for an oil that can give a factice with better physical characteristics at a reasonable price.

There are two types of factice, brown and white (3). Brown factice has been made by vulcanizing vegetable oil with sulfur at temperatures about 170°C. White factice on the other hand is vulcanized by sulfur monochloride at low temperatures, e.g. 10°C. The hardness and other physical characteristics of factice can be changed by varying the formulation. With brown factice types, higher sulfur levels give harder products. Certain fillers also harden the product, but also increase manufacturing costs.

Meadowfoam (*Limnanthes alba*) oil has over 95% unsaturated fatty acids (60% *cis*-5-eicosenoic acid, 10–20% *cis*-5-docosenoic acid and *cis*-13-docosenoic acid, 15–20% *cis*-5-*cis*-13-docosadienoic acid (4). The double bonds can be crosslinked with sulfur and therefore meadowfoam oil is potentially a good candidate to consider for factice production. The unique fatty acids of meadowfoam oil, having 90% of their unsaturation at the fifth carbon, may be a factor in increasing the chance of intra-molecular bonding (5,6), which may lead to a more compact, denser structure. Therefore, it may be harder, and, due to the decrease in the air volume in the polymer matrix, may break down more easily to form powder when force is applied. To pursue these ideas, color; acetone extract; free sulfur amounts; hardness and factice formation times of meadowfoam oil were compared to other industrial and potential vegetable oil factices.

EXPERIMENTAL

Materials and methods. The following commercial materials were used without further purification: Sulfur (sublimed), (Fisher Scientific Co., Fairlawn, NJ); sulfur monochloride, dicyclohexylamine, triethylamine, zinc oxide, magnesium oxide, sodium sulfite, cadmium acetate dihydrate, strontium chloride hexahydrate, ammonium bicarbonate, arsenic (III) oxide, 2-mercaptobenzothiazole, all reagent grade, were from Aldrich Chemical Co., Milwaukee, Wisconsin. Iodine, reagent grade, was from Matheson Coleman & Bell, Norwood, Ohio; potassium iodide, neutral and reagent grade, was from Mallinckrodt Inc., Paris, Kentucky, and TriSil-TBT was from Pierce Chemical Co., Rockford, Illinois. Refined meadowfoam oil was from Oregon Meadowfoam Growers Association, Salem, Oregon; rapeseed

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oil (refined) was from Ashland Chemical Co., Columbus, Ohio; and soybean oil (refined) was from Riceland Food Co., Stutgard, Alaska. The other oils were extracted from seeds and refined in Northern Regional Research Center Laboratories, Peoria, Illinois.

Gas chromatographic analyses of fatty acid methyl esters were conducted with a Hewlett-Packard 5890A GC, (Avondale, PA). A 25 m CP-Sil 84 column was used with a temperature program of 130–220°C at 2°C/min and a 15 min hold at 220°C. Fatty acid methyl esters were prepared by using catalytic amounts of sodium methoxide in methanol.

The vulcanization reactions were conducted in 400 mL beakers heated by an oil bath with a temperature control of ± 1°C. The reaction mass was blanketed with nitrogen until gel formed. Throughout all the experiments the same motor and stirring blade were used. The rotation rate of the stirrer blade was also kept constant and was adjusted to a speed that prevented sulfur from forming agglomerates bigger than 0.1 mm in diameter when added to the oil.

For production of brown factice the reaction mixture, excluding sulfur, was brought to reaction temperature. Sulfur was then added, usually in one min, to the mixing reaction mass. The start of sulfur addition was marked as time zero. After a drop of 5–8°C in reaction temperature due to the addition of sulfur, the temperature was brought back to reaction temperature, usually in 3 min. From then on the temperature was held constant at ± 1°C until the mass started to solidify. At this point, stirring and nitrogen flow were stopped, the oil bath was lowered, and the reaction mixture was left to cool to room temperature.

For production of white factice the same mixing system was used but the oil bath was exchanged with a cooling bath containing an ice-water slush. The reaction temperature was held at 10 ± 1°C. Sulfur monochloride was added to the reaction mixture at 10°C, in a steady trickle, in a span of 3 min. Again the reaction mass was blanketed with nitrogen. Stirring and nitrogen flow were stopped when the reaction mass started to solidify.

For ash analysis, one gram of sample was gently heated in a No. O porcelain crucible. When smoking had ceased the mass was ignited to constant weight. This weight was used to calculate the ash percent.

For free sulfur tests ASTM D297-50T method was used.

Acetone extract values were determined on a two-gram ground sample put in a 33 m × 94 mm extraction thimble, plugged with cotton, and placed in a Soxhlet extractor with 100 mL of acetone. Brown factice was extracted for 16 hr, and white factice was extracted for 8 hr. The mass of extracted material was calculated from the difference between the initial and final weights of the thimble and the results were reported as percent soluble material in acetone.

Hardness tests were done with a hand-held Shore Durometer, type A.

From one batch to another the variations of acetone extract values are ± 3%, of free sulfur values ± 0.5%, of hardness values ± 5 shore A units, and of gel time ± 5 min.

RESULTS AND DISCUSSION

In the first study, the hardness, acetone extract, free sulfur and ash values of the factices of various vegetable oils were compared as a function of the amount of sulfur used in the vulcanization. Table 1 shows the compositions, determined by gas chromatography, of the fatty acids of the vegetable oils. Analyses of the oils were in good agreement with the literature values for meadowfoam (7,8), rapeseed (7,8), crambe (7,8) castor (9), *Lesquerella* (10), and soybean oils (8).

Table 2 compares the physical properties of their factices. High erucic acid rapeseed oil is used in better quality factices because it provides a harder product in a shorter reaction time (1,12). Crambe oil, presently in commercial development, has fatty acids similar to rapeseed oil and was compared alongside it. *Lesquerella* oil, an experimental oil that contains C_{20} hydroxy fatty acids, was compared with castor oil because both have similar oxygenated fatty acids. Jojoba oil contains long

TABLE 1

Typical Compositions of Long Chain Fatty Acid Sources

				Jojoba[a]				
	Meadowfoam	Rape	Crambe	Fatty acids	Fatty alcohols	Castor[b]	*Lesquerella*[c]	Soybean
$<C_{18}$	0.5	2.5	2.3	2	0.1	1	1.6	10
18:0	—	1	1	—	0.2	1	1.9	4
18:1	1.4	14.5	16	15	1.1	3[a]	16.9	22
18:2	0.5	15.2	9	—	—	4.2	8	54
18:3	—	10	6	—	—	0.3	—	7.2
20:0	0.5	0.6	1	—	—	0.3	—	—
20:1 (Δ5)	64	—	—	—	—	—	—	—
20:1 (Δ11)	—	9.5	3.5	69	43.8	—	—	—
22:1 (Δ5)	3	—	—	—	—	—	—	—
22:1 (Δ13)	10	43	55	22	44.9	—	—	—
22:2 (Δ5,13)	19	—	—	—	—	—	—	—

[a] Values for this column were obtained from Reference 11.

[b] Contains 89.5% *cis*-12-hydroxyoctadec-9-enoic acid(ricinoleic acid 18:1)[9].

[c] Contains 52% 14-hydroxy-*cis*-11 eicosenoic acid (*Lesquerolic* acid 20:1)[10] and 2.9% 14-hydroxy-*cis*-11,*cis*-17-eicosadienoic (auricolic acid 20:2)[10].

TABLE 2

Physical Properties of Brown Factices Prepared at 180°C

Experiment number	Oil	Sulfur pho[a]	Gel time (min)	Shore A hardness	Acetone extract (%)	Free sulfur (%)	Ash (%)
1	Meadowfoam	30	15	45	10.5	3.5	trace
2	Rapeseed	30	15	30	23.3	3.8	0.06
3	Crambe	30	18	35	18.2	2.0	trace
4	Soybean	30	13	23	40.5	3.67	trace
5	Meadowfoam	20	19	35	24.7	1.1	0.004
6	Rapeseed	20	20	30	30.9	0.8	trace
7	Crambe	20	20	35	18.2	2.0	0.05
8	Jojoba[b]	20	—	—	—	—	—
9	Soybean	20	50	NA[c]	39.71	0.40	trace
10	Castor	20	31	32	65.7	1.93	0.04
11	*Lesquerella*	20	30	30	47.7	1.5	0.02
12	Meadowfoam	12	55	NA[c]	31.1	0.33	trace
13	Rapeseed	12	105	NA[c]	26.0	0.15	0.06
14	Crambe	12	75	NA[c]	36.3	0.09	trace
15	Meadowfoam	10	95	NA[c]	33.4	0.12	trace
16	Rapeseed	10	162	NA[c]	27.7	0.13	0.09
17	Crambe	10	125	NA[c]	26.7	0.24	0.05

[a] pho = Parts per hundred parts of oil.

[b] The reactions were stopped after 10 hr with no gel formation.

[c] = The factice was too soft. Hardness could not be measured with the shore A durometer.

chain wax-esters instead of triglycerides and is an excellent oil for manufacturing lubricants (7,8). However, as factice formation has been reported (13) it was included in this study with hopes of obtaining a factice with unusual properties.

In most commercial factices, soybean oil is preferred due to its low cost. However, it does require higher amounts of sulfur to form a gel. Therefore, these studies were started at 30 pho sulfur, and later the amount of sulfur was gradually decreased.

The formulations with 30 pho sulfur had very short reaction times. They also had a higher free sulfur content than the generally accepted 2%.

At 20 pho sulfur, meadowfoam oil; crambe oil; and rapeseed oil factices did not show much difference in their time of gelling. Soybean oil took a significantly longer time to gel, and produced a softer product with higher acetone extract values. Jojoba oil reaction was stopped after 10 hr of heating when the masses became very viscous but had not yet gelled. Castor and *Lesquerella* oils took a longer time to gel also, and especially castor oil, had high acetone extract values. Although meadowfoam oil, rapeseed oil and *Lesquerella* oil factices had somewhat similar acetone extract and free sulfur values, their differences might be significant when used in certain applications.

When the sulfur amount was lowered to 12 pho, meadowfoam oil gelled much faster than rapeseed or crambe oils, but had a higher free sulfur value.

At 10 pho sulfur, again meadowfoam oil gelled much faster than rapeseed or crambe oils producing a factice that had acetone extract and free sulfur values similar to the factices of rapeseed and crambe under these conditions. In addition to having a faster gelling time, meadowfoam oil gives a factice that is harder and much less sticky. This aspect may be of interest to manufacturers because a harder, non-sticky factice that can readily be powdered, will make handling during manufacturing and transportation much easier. It will also save a considerable amount of energy in cleaning the reactors.

When factice is put under pressure in a mill or in a mortar, it will either break into very small particles in the form of a coarse powder or it will take a fluffy form. If the factice is sticky, particles tend to stick to each other so much that the mass resembles masticated rubber, and does not break down to powder. This last form was frequently encountered with low amounts of sulfur. While meadowfoam oil factice with 10 parts of sulfur per hundred parts of oil gave the first form of non-sticky coarse powder, rapeseed and crambe seed oils gave this coarse powder only above 20 pho of sulfur. The ease in formation of powder in factice has proven very valuable in sample preparation and especially in cleaning factice from reactors and stirrers, and in handling and transportation.

The vulcanizations in Table 3 were run at 160°C. The decrease in the temperature increases the reaction time, and helps to amplify the difference between the oils. Lowering the temperature further from 160°C to 150°C resulted in almost doubling the reaction time in the few cases that were studied. Therefore 160°C and 20 pho of sulfur were chosen as the basic reaction conditions to compare results from different oils.

The reaction times, acetone extract and free sulfur values are about the same in meadowfoam oil, rapeseed oil and crambe oil factices at 160°C. However, meadowfoam factice is still harder and has a lighter color when compared to the others. Castor and *Lesquerella* oil factices have very high acetone extract and free sulfur values. Although soybean oil gelled as fast as rapeseed oil, at this temperature, it gave a soft and sticky product with a high acetone extract value.

Another advantage of meadowfoam oil is that it gives much lighter colored factices. This was especially noticeable in powder form. Rapeseed, crambe, castor, *Lesquerella* and soybean oils all gave factices ranging from black-brown to black-green while mead-

TABLE 3

Physical Properties of Brown Factices Prepared at 160°C[a]

Experiment number	Oil	Gel time (min)	Shore A hardness	Acetone extract (%)	Free sulfur (%)	Ash (%)
18	Meadowfoam	80	30	27.3	1.2	0.02
19	Rapeseed	90	19	22.2	1.4	trace
20	Crambe	100	23	31.6	1.5	trace
21	Soybean	85	NA[b]	41.8	0.39	trace
22	Castor	125	15	85	2.67	trace
23	*Lesquerella*	100	18	45.6	2.22	trace

[a] In all formulations the amount of sulfur was 20 pho.

[b] NA = The factice was too soft. Hardness could not be measured with the short A durometer.

TABLE 4

Physical Properties of White Factices at 10°C

Experiment number	Oil	S_2Cl_2 (pho)	Other additives (pho)	Gel time (min)	Shore A Hardness	Acetone extract (%)	Free sulfur (%)	Ash (%)
24	Meadowfoam	20	MgO (5)	26	45	6.2	0.11	4.31
25	Rapeseed	20	MgO (5)	70	38	8.3	0.30	4.01
26	Jojoba	20	MgO (5)	—	—	—	—	—

TABLE 5

Physical Properties of Brown Factices With Additives at 160°C

Experiment number	Oil	Other additives (pho)	Sulfur (pho)	Gel time (min)	Shore A hardness	Acetone extract (%)	Free sulfur (%)	Ash (%)
27	Meadowfoam	triethylamine (3.63)	20	80	28	16.50	1.35	trace
28	Rapeseed	triethylamine (3.63)	20	70	20	16.62	1.17	0.02
29	Meadowfoam	dicyclohexylamine (3.63)	20	75	40	27.58	1.24	0.01
30	Rapeseed	dicyclohexylamine (3.63)	20	69	30	30.58	1.00	0.03
31	Meadowfoam	zinc oxide (8)	15	194	7	29.78	0.25	6.5
32	Rapeseed	zinc oxide (8)	15	125	6	38.14	0.20	6.3
33	Meadowfoam	zinc oxide (10.3) steric acid (10.3)	20	127	15	32.81	0.83	7.35
34	Rapeseed	zinc oxide (10.3) steric acid (10.3)	20	97	10	38.06	0.80	7.5
35	Meadowfoam	iodine (0.3)	20	120	30	15.57	0.4	trace
36	Rapeseed	iodine (0.3)	20	85	27	24.14	0.9	0.02
37	Meadowfoam	2-mercaptobezothiazole (4.8)	20	90	18	17.35	0.84	0.005
38	Rapeseed	2-mercaptoebezothiazole (4.8)	20	90	18	47.58	1.16	0.02
39	Meadowfoam	magnesium oxide (9)	22	103	42	25.63	0.78	6.7
40	Rapeseed	magnesium oxide (9)	22	90	25	32.32	1.56	6.8

owfoam oil factices or factices from mixtures of oils containing meadowfoam oil were different shades of yellow. This was also the case with factices obtained at 160°C. The lightest colored factice was made with meadowfoam oil and dicyclohexylamine. This factice had an almost transparent amber color, with a golden yellow powder.

In the studies with white factice, the meadowfoam oil product showed better physical properties than rapeseed oil factice prepared under the same conditions. Hardness, acetone extract and free sulfur values were all much better, but the biggest difference was in the reaction time. Jojoba oil was also tried under the same reaction conditions, but the reaction was stopped after 24 hr when no gel formation could be seen. However, the reaction mass was very viscous at this time. These results can be seen in Table 4.

A few of the many accelerators and polymerization initiators that are used in the vulcanization reactions of rubber and vegetable oils were tried with meadowfoam and rapeseed oils.

Accelerators increase the rate of the sulfur combination by breaking down the stable form of sulfur, S_8, into sulfides and polysulfides, which then release sulfur in active form (14). Also they increase the efficiency and utilization of sulfur as a crosslinking agent and produce a simpler network structure. Accelerators can be inorganic, like zinc oxide with fatty acids, or organic in nature, such as aldehyde amines, guanidine, thiazole, thiuram, dithicarbamate, amine or xanthate (1). In this work, a few of these accelerators were used, such as magnesium oxide, which increases hardness and acts as a neutralizing agent in white factice (15,16), and iodine, which is an excellent agent to lower the free sulfur amount (17). The results are summarized in Table 5.

With the addition of amines, meadowfoam oil factice becomes much harder and lighter in color. The other properties closely resemble those of rapeseed oil factice.

Magnesium oxide was added to harden the product. With the addition of this accelerator, the resulting meadowfoam oil factice had a significantly higher hardness value with a lower acetone extract and free sulfur content.

Zinc oxide, used as an accelerator with or without fatty acids in rubber vulcanizations, did not reduce the reaction times of oil vulcanizations. However, there was a decrease in the free sulfur value. There was also a decrease in the hardness of factices. 2-Mercaptobenzothiazole, also an accelerator in rubber vulcanizations (14), gave similar results. Iodine, which is listed in the literature (1) as an excellent agent to reduce free sulfur values, did show the same effect with meadowfoam and rapeseed oils. Another advantage of iodine was the increase in the hardness of the factices. With iodine again meadowfoam oil factice showed better properties than rapeseed oil factice, but the reaction took a long time to complete.

From the above findings we can say that in addition to providing a good quality product, meadowfoam oil factice will bring economical advantages in reactor heating costs, mixing energy, manufacturing time, cooling time, equipment shutdown time for cleaning and ease of packaging and transporting.

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