

Factice from Oil Mixtures

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High-quality brown factice is produced from meadowfoam and rapeseed oils, while a poorer-quality factice is produced from soybean oil, a less expensive oil. A one-to-one mixture of soybean and meadowfoam or rapeseed oil produces a factice that has similar physical characteristics as factice produced from 100% meadowfoam or rapeseed oils. In addition, meadowfoam oil and rapeseed oil act as accelerators when mixed with castor or jojoba oils. White factice productions from soybean oil can also be improved when mixed with meadowfoam or rapeseed oils. The difference in cost, obtained by using as much as 50% soybean oil instead of the higher-costing oil, will translate into significant savings for the factice and rubber industries.

KEY WORDS: Castor, factice, jojoba, lesquerella, lubricant, meadowfoam, rapeseed, soybean.

Factice, used for more than a hundred years in the rubber industry, is made by vulcanizing unsaturated vegetable oils. When fatty acid chains in the oils are cross-linked with sulfur (brown factice) or with S_2Cl_2 (white factice), the oil gels to form a rubbery compound. This in turn is used in rubber mixes to give dimensional stability to extruded articles, to reduce mold fill time and cure cycle time, to improve ozone resistance of the rubber compound, to give a smooth velvety feel to rubber articles, to reduce migration of oils and plasticizers to the surface of low-durometer stocks, to absorb large amounts of mineral oil and liquid plasticizers on the mill and in the Banbury mixer and to have the ability to flow and promote flow under mechanical pressure (1). Its abra-deability makes it the main component in eraser formulations. Consequently, factice is of great value to the rubber industry for its functions in formulations and its low cost compared to raw rubber.

There are different quality factices, all of which have different application areas. The harder factices, which are lighter in color and have more desirable free sulfur and acetone extract values (2), are obtained from longer-chain fatty acid-containing vegetable oils such as rapeseed oil or meadowfoam oil. These factices also have superior behavior in rubber mixes compared to soybean oil factices (3). The higher cost of these oils, however, limits their use in the industry. Therefore, this study concentrates on ways to lower the cost but maintain the quality of factices made from long-chain fatty acid-containing vegetable oils.

EXPERIMENTAL PROCEDURES

Materials and methods. Refined meadowfoam oil was obtained from Oregon Meadowfoam Growers Association (Salem, OR); refined rapeseed oil was from Ashland Chemical Co. (Columbus, OH); and refined soybean oil was from Riceland Food Co. (Stuttgart, AR). The other oils were extracted from seeds and refined at the National Center for

Agricultural Utilization Research (Peoria, IL). Sulfur (sublimed) from Fisher Scientific Co. (Fairlawn, NJ), sulfur monochloride, sodium sulfite, cadmium acetate dihydrate, strontium chloride hexahydrate, ammonium bicarbonate, arsenic (III) oxide from Aldrich Chemical Co. (Milwaukee, WI) and iodine from Matheson Coleman & Bell (Norwood, OH) were used without further purification.

Gas-chromatographic analyses of fatty acid methyl esters were conducted with a Hewlett-Packard 5890A GC, (Avondale, PA). A 25-cm 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 from the oils by using catalytic amounts of sodium methoxide in methanol.

The vulcanization reactions were conducted in 400-mL beakers heated by an oil bath with temperature control of $\pm 1^\circ\text{C}$. The reaction mass was blanketed with nitrogen until gel formed. The same motor and stirring blade were used throughout all experiments. 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 1 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. Then the temperature was held constant at $\pm 1^\circ\text{C}$ 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.

White factice was produced by using the same mixing system, but the oil bath was exchanged with a cooling bath containing an ice-water slush. The reaction temperature was held at $10 \pm 1^\circ\text{C}$. 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. 0 porcelain crucible. When smoking had ceased, the mass was ignited to constant weight. This weight was used to calculate the ash percent. Free sulfur and acetone extract values were determined by ASTM D 297 50T Method and ASTM D 297 24 Method, respectively (4). Hardness tests were done with a handheld Shore Durometer, Type A.

RESULTS AND DISCUSSION

In our studies, soybean oil gelled slowly, forming a factice that was sticky, soft and dark in color. Our hope was to improve the quality of soybean oil factice by mixing soybean oil with rapeseed or meadowfoam oils, and then to form factice. Brown factice made from a 50:50 mixture of meadowfoam and soybean oils gelled at the same time as pure meadowfoam oil factice (Table 1). Rapeseed oil

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TABLE 1
Physical Properties of Brown Factices^a

Oil	Percentage in mixture	Gel time (min)	Shore A hardness	Acetone extract	Free sulfur (%)
Soybean	100	50	NA ^b	37.0	0.40
Meadowfoam	100	19	35	24.7	1.1
Rapeseed	100	20	30	30.9	0.8
Soybean + meadowfoam	50:50	19	25	25.1	0.58
Soybean + rapeseed	50:50	21	30	33.1	0.87
Soybean + meadowfoam	70:30	29	23	26.9	0.53
Soybean + rapeseed	70:30	27	19	36.7	0.44
Soybean + meadowfoam	85:15	29	13	30.0	0.42
Soybean + rapeseed	85:15	30	13	33.0	0.71

^aFactices were prepared with 20 parts of sulfur per hundred parts of oil at 180°C (2).

^bNot applicable, was too soft to be measured.

mixture behaved similarly to meadowfoam oil, giving a factice that gelled almost at the same time with pure rapeseed oil. The hardness and acetone extract values of these factices were also much closer to the pure factices from the longer-chain fatty acid-containing oils, especially for the meadowfoam and soybean oil mixture. In all mixtures the free sulfur values were below 2.0%, which is considered acceptable by the rubber industry. Factices that contain more than 2% free sulfur may contribute too much sulfur into a rubber mixture, which already has low amounts of this compound. This significant excess will change curing times substantially, leading to the overcure of items that are vulcanized.

Batch-to-batch variations of acetone extract values are $\pm 3\%$, of free sulfur values $\pm 0.5\%$, of hardness values ± 5 shore A units and of gel time ± 5 min. According to these results, 50:50 mixtures of these oils produce practically the same quality factice that would be otherwise obtained from pure rapeseed or meadowfoam oil. The usage of mixtures will enable the factice industry to substantially lower manufacturing costs (5).

When percentage of soybean oil in mixtures increases, even to 85%, gel time, shore A hardness and acetone

extract values still retain characteristics that resemble pure meadowfoam and rapeseed oil factices. The free sulfur values also remain in the acceptable range.

Castor oil, seldom used today in factice production, gives a product that has high acetone extract and free sulfur values (Table 2). Lesquerella oil, similar to castor oil but containing less hydroxy fatty acids, also has high acetone extract and free sulfur values (2). When mixed with meadowfoam or rapeseed oils, in the case of lesquerella, the results did not change significantly. However, acetone extract and free sulfur values for castor oil decreased enough to be of interest to manufacturers.

Jojoba oil, a wax ester, does not gel under these conditions although it contains unsaturated fatty acids (2). Even a 30% jojoba oil mixture with 70% rapeseed or meadowfoam oil does not gel. However, 50:50 mixtures of the above oils did form factice with reasonable values. In this case, meadowfoam oil had an advantage because it formed gels much faster than rapeseed oil. Jojoba oil is used in lubricant production, sometimes with other oils (6-8). Therefore, we thought that its gelling with 50% mixtures of long-chain fatty acid-containing oils would be of interest to lubricant manufacturers.

TABLE 2
Physical Properties of Brown Factices^a

Oil	Percentage in mixture	Gel time (min)	Shore A hardness	Acetone extract	Free sulfur (%)
Lesquerella	100	30	30	47.7	1.5
Castor	100	31	32	76.5	2.29
Jojoba	100	Did not gel			
Meadowfoam	100	19	35	24.7	1.1
Rapeseed	100	20	30	30.9	0.8
Castor + meadowfoam	50:50	23	30	60.0	1.55
Castor + rapeseed	50:50	25	29	57.4	1.58
Castor + meadowfoam	70:30	26	30	63.6	1.94
Castor + rapeseed	70:30	26	28	66.7	2.10
Lesquerella + meadowfoam	50:50	27	30	47.7	1.8
Jojoba + meadowfoam	50:50	34	14	27.5	0.46
Jojoba + rapeseed	50:50	55	12	27.6	0.52
Jojoba + meadowfoam	70:30	Did not gel			
Jojoba + rapeseed	70:30	Did not gel			

^aFactices were prepared with 20 parts of sulfur per hundred parts of oil at 180°C (2).

FACTICE FROM OIL MIXTURES

TABLE 3

Physical Properties of White Factices^a

Oil	Percentage in mixture	Gel time (min)	Shore A hardness	Acetone extract	Free sulfur (%)
Meadowfoam	100	40	45	3.2	0.05
Rapeseed	100	90	38	5.1	0.2
Soybean	100	Did not gel			
Soybean + meadowfoam	50:50	130	20	13.2	0.08
Soybean + rapeseed	50:50	120	25	18.8	0.05
Soybean + meadowfoam	20:80	8 h ^b	5	24.5	0.06
Soybean + rapeseed	20:80	8 h ^b	NA ^c	24.3	0.1
Rapeseed + meadowfoam	10:90	97	45	2.3	0.08

^a Factices were prepared with 20 parts of sulfur monochloride per hundred parts of oil at 10°C (2).

^b Gel time listed in hours.

^c Not applicable, was too soft to be measured.

White factice is produced at lower temperatures and is used in cold-cure rubber formulations (1), it is commercially manufactured from long-chain unsaturated fatty acids, mainly rapeseed oil and it is currently imported into the United States. In Table 3 the same trend, seen in brown factice, is seen in white factice. Soybean oil by itself does not gel, whereas mixtures of soybean oil and meadowfoam or rapeseed oils do gel with as much as 80% soybean oil in the mixture. However, the hardness and gel times are much more acceptable with 50:50 mixtures. Therefore, it is possible to prepare a suitable mixture that gives the desired properties and still will cost less than using 100% rapeseed or meadowfoam oils.

A 10:90 mixture of meadowfoam and rapeseed oils (Table 3) gave a factice that also could be of interest to manufacturers. This mixture produced a factice that retained the hardness of 100% meadowfoam oil factice, and even though it doesn't show improvement in gel times, it

does have significantly lower acetone extract values than either rapeseed or meadowfoam oil white factices.

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