Isano Oil, a Conjugated Triple Bond Glyceride

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ISANO OIL is a radically different vegetable oil. Its fatty acids have conjugated acetylenic bonds, a terminal ethylenic bond, and an hydroxyl group. Isano oil, also called boleko oil or ongokea oil, is derived from the nut of the Olacaceae family, Onguekoa Gore Engler specie. Although it has been known for more than 60 years, commercial development of the oil has been slow because its properties and complex chemical structure have only recently become understood. This paper will review briefly the major published work on this oil to date and discuss its current commercial status and potential.

Commercial Status

The trees which bear the isano nuts grow abundantly in the Belgian and the French Congo. Over the years about 5,000 tons of nuts have been collected, which is roughly equivalent to 1,250 tons of oil. Capacity for reducing more than 100 tons of oil per month is now available, and it is reported that 10,000 tons of oil are potentially available each year. This tonnage puts the oil beyond the laboratory curiosity stage. Its lack of commercial availability to date as well as its dark color and high free fatty acid have discouraged large-scale development. Its price which ranges around the 25-cents-per-pound level is sufficient to pay for collection of the oil-bearing nuts and low enough to warrant industrial development. Because of the low value of by-products it is more economical to convert these oil-bearing nuts into oil at the origin than to export them. The nut is made up of about one-third shell and two-thirds kernels. The kernels contain 60% oil and 40% of a by-product meal, which is used only as a fertilizer. The kernels cannot be exported because of the build-up of free fatty acid after the nuts are broken and before the oil is expressed from the kernels. The present method of oil production uses the continuous screw press.

Isano oil was studied as early as 1896, at which time industrial applications were foreseen. It is not yet an industrial oil of significant volume because it has some peculiar properties. For example, it explodes when heated sufficiently. It is an extremely unsaturated oil, yet it does not dry. Also the oil darkens with mild heat or on sufficient exposure to light.

Composition

Isano oil is a mixture of glycerides of highly unsaturated fatty acids. Present in greatest amounts are isanic and isanolic acids, both of which contain conjugated triene linkages. Steger and Van Loon (15), Boekenoogen (4) and Castille (5) discovered the nature of the unsaturation of isanic acid, $C_{18}H_{26}O_2$, one of the principal fatty acids. The molecular weight of isanic acid has been reported as 274, as determined by cryoscopic methods using benzene and acetic acid (9). DeVries (7) described a method for extracting isanic acid from isano oil and found that it constitutes about 46% of the oil:

In 1940 the structure of isanic acid was proven to be (16):

$$CH_2 = CH(CH_2)_4\,C \equiv C\,C \equiv C\,(CH_2)_7CO_2H$$

Isanic acid, also called erythrogenic acid, has been synthesized (3), and its absorption spectrum reported (2).

The high acetyl value of isano oil is the result of an hydroxy unsaturated acid with the hydroxy group on the eighth carbon (13). Kaufman (10) isolated the hydroxy fatty acid, which he termed isanolic acid and identified it as

$$CH_3(CH_2)_2CH = CHC \equiv CC \equiv \\ CCH_2CH(OH)(CH_2)_6COOH$$

He estimated that isano oil contained about 44% isanolic acid.

Seher (14) found a new fatty acid, about 9% of the isano oil, by means of paper chromatography and named it bolekoic acid. He also verified the structure of isanic and isanolic acid by using ultraviolet absorption spectra.

Physical and Chemical Constants

Isano oil is a mildly pungent, viscous, golden yellow liquid which turns dark on exposure to light or heat. Table I lists its physical and chemical constants. An average range of values and the analysis of a recent large commercial lot obtained from an expelling operation in Africa are given. Commercial oil is darkened by the heat generated by the screw press. Oil obtained from nuts by laboratory extraction is about 10 Gardner. Isano oil is soluble to only a limited degree in petroleum ether, ethanol, and hexane but is completely miscible with benzene, acetone, ethyl ether, carbon tetrachloride, and chloroform.

TABLE I

Physical and Chemical Constants of Isano Oil

	Average range	New commercial lot
Saponification value	185–200	191
Specific gravity 25/25°C.	0.977–0.980	0.978
Refractive index 25°C.	1.505–1.509	1.508
Acetyl value	65–85	79.1
Viscosity 25°C. (U-W Gardner)	7–10 poise	9
Unsaponifiable, %	0.5–5	0.86
Iodine value	316[a]	230[b]
Free fatty acid, %	5–25	7
Color (Gardner)	10–18	12

[a] Hydrogenation iodine value.

[b] Wijs method with excess reagent and overnight standing before titration.

The degree of unsaturation of isano oil is not accurately measurable by the Wijs or Hanus iodine value methods because of the conjugated triple bonds. Early literature varies widely on iodine values because of the methods and conditions used and because of an indefinite endpoint. We found that a modification of the Wijs method, in which approximately three times the theoretical amount of reagent was used, and overnight standing before titration gave fairly reproducible results. The theoretical iodine value as determined by hydrogenation (8) is 316.

The shell of the isano nut protects the meat, but after the nut is broken, deterioration sets in rapidly, as evidenced by a rise in free fatty acid. However, once the oil is obtained, the free fatty acid content is stable. The high specific gravity, viscosity, and affinity for water of isano oil make refining or degumming of it difficult. The viscosity of isano oil changes little in storage. A sample more than four years old was found to have U-viscosity, well within the normal range. In an accelerated test, oil held at 40°C. for 45 days did not change in viscosity, acidity, or color.

Chemical Properties

The triene type of unsaturation in isano oil makes it quite reactive; however this reactivity is a different type than that of the more common ethylenic oils. For example, isano is more unsaturated than linseed or wood oil, but it does not dry to a firm film.

It was found that hydrogen adds stepwise to isano oil, first completely saturating one triple bond, then saturating the other (14). Chlorine also adds readily and exothermically. In one test 1,009 g. of oil increased by 403 g. when chlorine was bubbled through the oil at room temperature until no more was absorbed. Isano oil can be acetylated by normal procedures. The acetylated oil has the same explosive exothermic reaction as the crude oil. Tolylene diisocyanate reacts with isano oil to form a viscous polymer which dries to a hard film. Careful temperature control is necessary when sulfur is reacted with isano oil at temperatures above 150°C.

The dark color of isano oil is inherent because of a chromophore configuration, therefore adsorptive agents have no effect on its color. Crystals of both synthesized and natural isanic acid turn red on exposure to daylight (3). Either heat or light will change the yellow color (about 10 Gardner) of fresh oil to a dark red-brown (18 Gardner).

Effect of Heat

One of the outstanding properties of isano oil is its explosive nature when heated under certain conditions. But the conditions which lead to explosion are not fully described in the technical literature. To explode, isano oil requires a) a restricting container, b) adequate air, and c) sufficient heat. Needless to say, extreme caution is recommended when working with isano oil above 200°C. with or without an inert atmosphere. The effect of heat was studied as follows: 50 g. of isano oil in an open 28-mm. x 200-mm. test tube were placed in an oil bath maintained at 178°C., 200°C., and 223°C. for different periods of time. The changes in the oil characteristics are recorded in Table II. It is interesting to note the relatively small decrease in apparent iodine value, even after considerable polymerization has taken place, as evidenced by the large increase in viscosity. Under these conditions of heat treatment a violent exothermic reaction took place after the oil gelled, with evolution of heavy white fumes.

TABLE II
Effect of Heat on Isano Oil[a]

Heating conditions	Refractive index 25°C.	Viscosity 25°C. (poise)	Iodine value [c]	Specific gravity 25/25°C.	Free fatty acid,%
178°C. 1 hr.	1.5097	9.5	220	0.978	6.3
178°C. 2 hrs.	1.5107	15.4	219	0.981	5.4
178°C. 9½ hrs.[b]	1.5152	130	......	0.990	5.5
200°C. 15 min.	1.5087	10.7	220	0.979	7.6
200°C. 65 min.	1.5120	22.7	214	0.984	7.1
200°C. 130 min.[b]	1.5158	390	206	0.985	6.1
223°C. 15 min.	1.5112	12	218	0.979	7.6
223°C. 25 min.	1.5124	20	216	0.982	7.4
223°C. 40 min.[b]	1.5164	390	208	0.987	6.4

[a] The original oil had refractive index 25°C. 1.5074, viscosity 25°C. (poise) 6, iodine value 230, specific gravity .978, free fatty acid 7.7.

[b] Gelation took place at 178°C. in 10 hours, at 200°C. in 150 minutes, at 223°C. in 55 minutes, at 233°C. in 20 minutes.

[c] Wijs method with excess reagent and over-night standing before titration.

Explosion did not take place when nitrogen or carbon dioxide were passed through the oil before and during immersion in the bath at 235°C. After the oil gelled and stopped the flow of gas, the exothermic reaction took place with a temperature rise up to 310°C. but without evolution of heavy white fumes. In this case the gel stayed in the test tube whereas, when no inert gas was used, evolution of gases forced the gel out of the tube. No explosive reaction occurred even though the gelled isano oil was held at 235°C. for 8 hrs. The resultant gel was quite hard but showed no carbonization, which was found when inert gas was not used.

Uses

One of the most interesting applications of isano oil is in fire-resistant coatings. The exothermic reaction and evolution of gas, described above, led to the use of isano oil as an intumescent vehicle in fire-resistant coatings. When a surface coated with a paint which contains raw isano oil and a drying oil is exposed to sufficient heat, the exothermic reaction set off causes the film to swell by the evolution of gases, thus providing a protective insulating layer. Isano oil can be mixed with the linseed oil to provide an excellent drying vehicle. This vehicle, formulated with fire-retarding pigments and extenders, makes a paint of good dry, excellent water-resistance and intumescent characteristics. A complete study which includes formulations, exposure data, and fire-loss characteristics is found in a published report, "Development of Fire-Retardant Paints and Paint Systems," U. S. Department of Commerce, Office of Technical Services, Report No. Pb 111939. This report was prepared by Harvey Miller of the Engineer Research and Development Laboratories for the U. S. Army Corps of Engineers. This work on isano oil was done under a research contract with the Vita-Var Corporation. The patent (1) covering this development may be used free of charge by any manufacturer supplying the U. S. government. One of the conclusions of this report is that "the best fire-retardant exterior paint which we have produced is EX No. 20." The final report (17) gives the formula for EX No. 20 as follows:

EXTERIOR PAINT EX NO. 20

Pigment—61%	Titanium dioxide	10.30
	Zinc borate	30.00
	Blanc fixe	15.20
	Lead sulfate	17.35
	Lead carbonate	17.35
	Zinc oxide	9.80
		100.00
Vehicle—39%	Nonvolatile varnish-makers' linseed oil	27.20
	Isano oil	27.20
	Chlorinated paraffin 70%	11.10
	Polyamide resin No. 93	10.20
	Volatile	21.70
	Driers	2.60
		100.00

PVC	40%
Wt./Gal.	15.9 lbs.
Viscosity	98 Ku
Grind	1

Drying Characteristics

M. Fauve (9) has described at length the effects of heat treatment of isano and its drying properties, and the drying properties of various blends with other oils. For example, he reported improved drying, better water-resistance, superior pigment wetting, higher gloss, and better flowing properties with an 80:20 linseed-isano blend. In the various drying tests we have observed, only in the case of the unusually thick film reported below, that the speed of drying was improved by adding isano oil to a drying oil. However blends of linseed and safflower each with 20% isano oil and with driers (0.24% Pb, 0.03% Co, and 0.015% Mn) dried on tin panels for 72 hrs. and submerged in water at room temperature showed markedly better water-resistance than did the pure oils. However the water-resistance of the isano-linseed blend was not as good as that of the safflower control. Hot-water resistance was similarly improved. The 80:20 safflower-isano blend with anthraquinone catalyst added was heat-bodied to Z5 in 3 hrs. at 260°C., whereas pure safflower oil similarly catalyzed requires about 18 hrs. at 288°C. to reach Z5. The safflower-isano bodied oil was extremely dark, and films of it had very poor caustic resistance.

In another laboratory careful observations were made of the influence of isano on the drying of linseed oil. These observations are reported in Table III. It is evident that the 80:20 linseed-isano blend dries more slowly but makes a harder, significantly more water-resistant film than does linseed oil alone. It is interesting to note that when thicker films were formed, the drying relationship was reversed. For example, a film of nonbreak linseed oil 0.039 in. thick thickened but did not dry in 264 hrs. whereas the 80:20 linseed-isano blend of the same thickness was dry to touch. The refractive index of the blend had increased from 1.4861 to 1.4896 just prior to drying whereas the linseed had changed only from 1.4800 to 1.4820.

TABLE III

Comparison of Isano-Linseed Oil and Pure Linseed Oil Films

	Nonbreak linseed oil	80:20 Linseed-isano	Nonbreak linseed with driers[a]	80:20 Linseed-isano with driers[a]
Dry to touch (hrs.) (film thickness 0.00075 in.)	121	136	6.2	7.3
Hardness at above dry times	Imprint and mars	No imprint, no mar	Imprint and mars	No imprint, no mar
Oil ground with 35% Rutile–TiO_2 film thickness 0.00075 in. dry to touch (hrs.)	......	......	4.5	5.5
Hardness			Imprint and mars	No imprint, no mar
Immersion: Films flowed on glass, held 50°C. for 14 hrs. under cold water 8 hrs. 16 hrs. recovery	Permanently white	Slightly white	Slightly white	No white

[a] Driers used: 0.24% Pb, 0.03% Co, 0.015% Mn as metal.

Isano oil has been cooked with familiar varnish resins (ester gum, dammar, copal ester, phenol resin) and yielded dark products with greatly improved water-resistance (9). A drying oil has been made by heating isano oil and a varnish constituent together or by heating an oil other than isano and cobodying with it (12).

Other Applications

As would be expected of its constituent isanolic acid, isano oil reacts with tolylene diisocyanate to yield a product with drying properties. The viscous oil obtained by reacting 15 parts of tolylene diisocyanate with 100 parts of isano oil at 130°C. dried in 24 hrs. to a tack-free film having gloss, good water proofness, and flexibility. In our laboratory a similar experiment was conducted by adding 12 g. of tolylene diisocyanate dropwise with stirring to 100 g. of isano oil at 130°C. The resultant product was dark, greater than Z10 viscosity, and dried to a slightly tacky film. Urethane foams can be made in the usual fashion by the addition of a diisocyanate to isano oil, followed by curing with an amine. The few foams which were made were inferior, possibly because of insufficient concentration of hydroxyl groups in the oil.

Sulfur chloride reacts with isano oil to form an excellent factice (9). These elastic products were stated to be markedly superior to the oil factices used in the rubber industry in regard to their miscibility, curing, aging, and general workability. This exothermic reaction is best carried out at 35°C. with about 7% sulfur chloride.

Another reaction (6) with an alkyl phenol and subsequent polymerization with formaldehyde produced a resin, which when reacted with ethylene oxide, made a product reportedly useful in breaking oil-field emulsions.

Summary

Isano oil is now commercially available. Its major constituent fatty acids, isanic and isanolic acid, are unusual in their reactivity because of a conjugated acetylenic bond system in the middle of an 18-carbon chain. When heated sufficiently, the oil reacts exothermically with violence. This property has useful application in fire-retardant paints. Other uses and chemical reactions are given.

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REFERENCES

1. Allen, A. O., Murray, T. M., and Liberti, F. (Vita-Var Company), U. S. 2,754,217 (1956).
2. Armitage, J. B., Cook, C. L., Entwistle, N., Jones, E. R. H., and Whiting, M. C., J. Chem. Soc., 1998 (1952).
3. Black, H. K., and Weedon, B. C. L., Chem. and Ind. (London), 40 (1953).
4. Boekenoogen, H. A., Fette u. Seifen, *44*, 344 (1937).
5. Castille, A., Ann., *543*, 104 (1939).
6. DeGroote, M., and Keiser, B. (Petrolite Corporation), U. S. 2,568,118–9 (1951).
7. DeVries, E. (Union Chimique Belge), U. S. 2,789,993 (1957).
8. Eckey, E. W., "Vegetable Fats and Oils," p. 394, Reinhold Publishing Corporation (1954).
9. Fauve, M., Peintures pigments vernis, *24*, 147, 183, 209, 246, 281 (1948). This article partially reproduced in Official Digest No. 288, 38 (1949).
10. Kaufman, H. P., Baltes, J., Herminghaus, H., Fette u. Seifen, *53*, 537–542 (1951).
11. Muller, E. (Leverkusen-Bayerwerk), Ger. Pat. 828,577 (1949).
12. Priester, R. (N. V. Industrieele Maatschappij), U. S. 2,228,154 (1941); U. S. 2,280,082 (1942).
13. Riley, J. P., J. Chem. Soc., 1346 (1951).
14. Seher, A. von, Ann., *589*, 222 (1954).
15. Steger, A., and Loon, J. van, Fette u. Seifen, *44*, 243 (1937).
16. Steger, A., and Loon, J. van, Rec. trav. chim., *59*, 1156 (1940).
17. U. S. Department of Commerce, O.T.S. Report PB 111939 ($3.25), 121-page booklet, "Development of Fire-Retardant Paint and Paint Systems" (1952).

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