

# Erucamide<sup>1</sup>

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## ABSTRACT

Erucamide has, to a great extent, replaced the use of oleamide because of its higher mp and higher heat resistance. These properties are desirable because of the higher operating temperatures of newer polymers. Various derivatives are discussed, such as N-stearyl erucamide, which has a still higher mp and greater thermal stability. This type of product is used principally as a slip additive, an antiblock agent, and for paper-coating compositions and water-proofing. Erucamide and some of its derivatives are approved for use in polymers at low concentration levels. At these levels, the material is effective without adversely affecting other physical characteristics of the polymer. A summary of the literature is presented, including a review of some of the patents. Size of the market also is discussed.

## INTRODUCTION

Erucic acid is the principal raw material in making erucamide. Erucic acid is a *cis*- $\Delta^{13}$ -monounsaturated acid having mp 33-34 C and bp 169-170 C at 1 mm pressure. It also is known as *cis*-13-docosenoic acid.

Erucic acid occurs in seeds in the form of a glyceride. The chief source of erucic acid has been rapeseed oil. The amount of erucic acid contained in rapeseed oil varies according to species and cultivars. For example, the rapeseed grown in Canada (chiefly *Brassica campestris*) contains 20-40%, typically 25%, erucic acid in the form of its glyceride, while the European rape (*Brassica napus*) contains 45-55% erucic, typically 50% (1).

The other components of rapeseed oil are glycerides of linoleic, linolenic, and oleic acids, as well as some saturated acids. Yet another source (2) gives the typical composition of rapeseed oil shown in Table I.

The presence of polyunsaturated acids and their amides in erucamide is undesirable, particularly for use as a slip or antiblock additive in polymers.

In recent years a great deal of work has been done by the U.S. Department of Agriculture (USDA) (3,4) on the development of crambe seed. Crambe is a cool season crop, and it is adaptable as a spring crop to much of the wheat growing area of the Midwest and upper Midwest. The erucic acid content of crambe oil is 55-60%, with less oleic and considerably less polyunsaturates—only ca. 7%—than are present in rapeseed oil. Erucic acid even occurs in marine oil, as in herring, and to a much greater extent in nasturtium seed oil but not in animal oils. The development, hopefully, of crambe as a large crop in the U.S. may make the U.S. independent of foreign sources for erucic

acid. A further result of an American crambe crop would be an independent source for products such as brassylic acid and nylon 1313.

## MATERIALS AND METHODS

Erucamide normally is manufactured by reacting purified erucic acid at elevated temperatures and pressure with ammonia. The fatty acid mixture obtained either from crambe or rapeseed is purified to contain a high percentage of erucic acid (minimum 94-95%), with a low percentage of polyunsaturates not to exceed 2%, of which no more than 1% is C<sub>18</sub>.

The preferred temperature is below 200 C, and a fair operational pressure is 125-150 psi. The amidation is continued with periodic removal of water that is formed as a result of the reaction until the free fatty acid content of the reaction mixture is below 3%. If the temperature is elevated, the undesirable by-product, nitrile, is formed.

Further purification of the material is affected by either vacuum distillation of the mixture in a so-called wiped film evaporator, or by solvent extraction, or by crystallization.

Another procedure used to synthesize the amide involves transesterification of the glyceride of the fatty acid with methanol and subsequent treatment of the methyl ester with ammonia without the necessity of using pressure. This procedure produces an undesirable product because it contains some of the methyl ester, which imparts softness and tackiness to the material. Also, by this process, there is formation of the *trans*-material from the naturally occurring *cis* substance.

## PATENT LITERATURE

There are numerous patents issued which involve erucamide. One of the most important is Union Carbide's U.S. Patent 2,956,035, with corresponding patents in Germany and England, dealing with unblocking in polyolefin films. There is a U.S. Patent 3,562,291 assigned to Fine Organics, Inc., entitled "Instantaneous Friction-Reducing Additive for Polyethylene, Polypropylene, and Their Copolymers." It concerns a fast-acting slip additive with a mixture of lauramide and erucamide and is sold under the name Slip Quick.

There are patents on derivatives of erucamide, such as Spencer (now Gulf) Chemicals' N-oleyl erucamide slip agent in polyethylene compositions, U.S. Patent 2,991,265. Eastman Kodak has U.S. Patent 3,165,492 on "Polyalpha-monoolefin Films Containing N,N'-alkylenebisamides."

Continental Can has British Patent 1,000,178 on "Vinyl Plastisol Gasket Compositions." In this, erucamide provides controlled frictional seizure.

There is a Netherlands Patent 6,500,695 to ICI covering erucamide and other amines as additives to antistatic polyolefin films. A Dow Netherlands Patent 6,402,710 covers the addition of fatty acid amides to vinylidene chloride polymer films for antiblocking. Union Carbide has Netherlands Patent 6,511,088 on antiblocking additives for polyurethanes. Then there is Mobil's Netherlands Patent 6,516,448 on paper coating compositions. Mobil also has U.S. Patent 3,362,839 on wax coatings with good slip properties, using as additives N-oleyl palmitamide or N-stearyl erucamide.

There are many more, such as formaldehyde polymers stabilized by amides (U.S. Patent 3,330,801 to Stami-carbon); National Distillers British Patent 1,113,082 on ethylene-vinylacetate copolymer films with improved slip

<sup>1</sup>One of 12 papers presented in the symposium "Novel Uses of Agricultural Oils" at the AOCS Spring Meeting, New Orleans, April 1973.

TABLE I

Typical Composition of Rapeseed Oil

Components	Percent
Erucic acid	51.5
Polyunsaturates, principally in the form of linoleic and linolenic	ca. 22.0
Monounsaturated (other than erucic) in the form of oleic acid	ca. 20.0
Various saturated acids	6.5

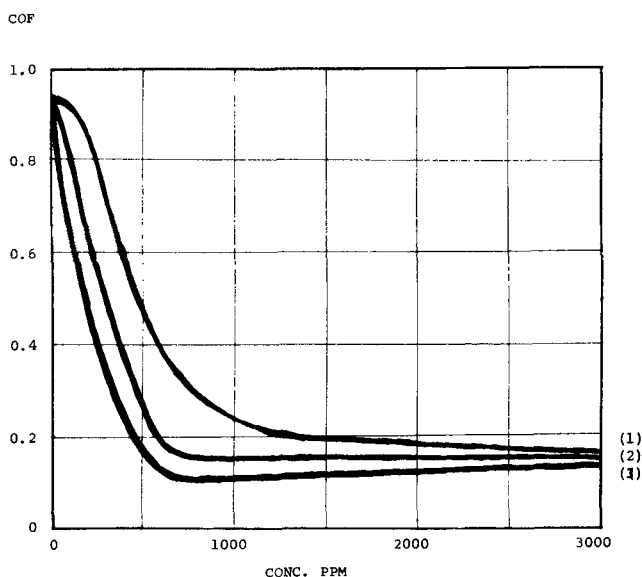


FIG. 1. Coefficient of friction (COF) vs. concentration for stearamide (1), erucamide (2), and oleamide (3).

properties containing fatty acid amides, including erucamide; vinyl resin plastisol compositions containing mixtures of unsaturated fatty acid amides (W.R. Grace, U.S. Patent 3,400,094); and polyethylene compositions with reduced coefficient of friction, with N-(2-hydroxyethyl)-*cis*-13-docosenamide (Dow U.S. Patent 3,396,137). Various foreign patents corresponding to the American have been issued on erucamide or derivatives thereof.

Mobil Oil has U.S. Patent 3,551,371 on strippable temporary coating compositions. There is U.S. 3,576,649 to Milprint on plastic package for electrically nonconductive material. This uses a mixture of erucamide and oleamide. Even the USDA has a patent in the field. This is 3,584,030 on N,N-disubstituted amides as plasticizers for vinyl resins.

## DISCUSSION

Erucamide's principal use is as an additive to alter the physical characteristics of polyethylene, polypropylene, and other polymers. The last published U.S. Tariff Commission report shows sales of 2,562,000 lb at a unit price of ca. \$1.00/lb (5). It has been estimated that 11,000,000 lb fatty acid amides were used for this application, of which erucamide is a significant portion (6).

Erucamide is allowed to be used in films as a non-blocking agent (7); N-stearyl erucamide is a permitted release agent in resins that may be in contact with food (8).

The single largest end use for erucamide is as a polymer additive, although there are a number of other interesting applications, as, for instance, in areas where a dry lubricant is desirable and in printing inks. Slip and antiblocking additives are required to improve handling of polyolefin film and bags on both manual and automatic packaging lines. Fatty acid amides emerged from a large number of additives as the most efficient and economical means of reducing surface friction and blocking properties, particularly in low density polyethylene. Among these, the saturated and monounsaturated amides with a chain length of 18-22 carbon atoms were found to be the most effective.

To accomplish the effect, the additive must be: a solid at room temperature, a stable liquid during extrusion of the resin, noncorrosive, nontoxic, effective at low concentrations, incompatible or insoluble in the resin, not adversely affect physical characteristics of film, such as strength, transparency, printability, and heat sealing.

In practice, the additive is blended into the resin and melts along with the plastic while in the extruder. As the

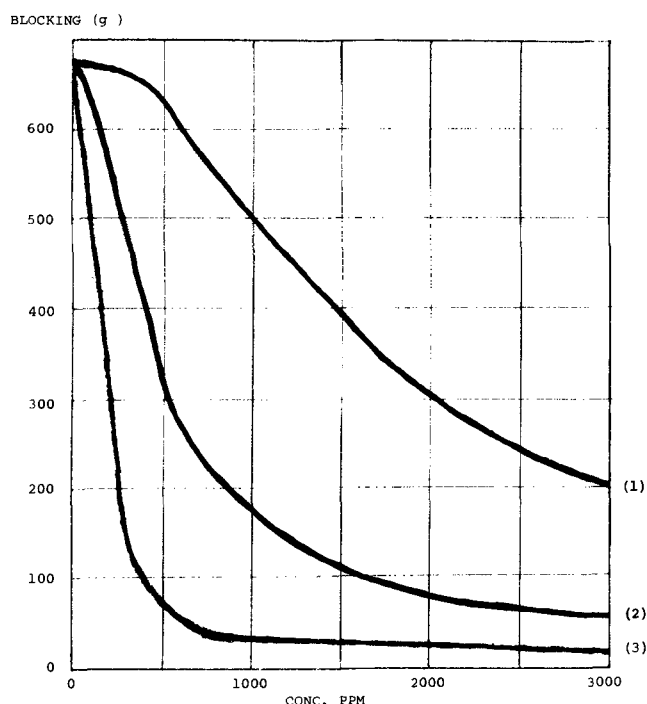


FIG. 2. Blocking vs. concentration of oleamide (1), erucamide (2), and stearamide (3). Higher blocking indicates more force required to pull apart two test sheets of film containing the amide additive.

plastic leaves the die and changes from a liquid to glass, it contracts in volume by 12-17%. At this moment, the fatty acid amide begins to exude, or bloom, to the surface in random aggregates, leaving microscopic bumps to produce a slip and antiblock effect.

It has been determined that, in general, saturated fatty acid amides, such as lauramide and stearamide, produce antiblocking properties, whereas monounsaturated amides provide slip. These functions have been studied in detail to determine where optimization occurs. Using an unmodified polyethylene resin having a density of 0.923, melt index of 1.0, and blown in 1-1/4 m thickness, the results obtained with oleamide, erucamide, and stearamide for slip vs. concentration are shown in Figure 1.

Coefficient of friction (COF) values of 0.8-1.0 would be considered no slip; 0.4-0.7 would be low; 0.2-0.4 medium; and 0-0.02 high slip.

Tests were run using American Society for Testing and Materials Method D-1894 (9). As can be seen, oleamide at ca. 700 ppm based upon wt of the resin provides the best results, followed closely by erucamide. Stearamide is the least effective, requiring a much higher concentration.

Figure 2 shows the results obtained on blocking vs. concentration of the same additives. The higher the value in g indicates more force required to pull apart two sheets of film. In this case, as was expected, stearamide, a saturated amide, provides the best results. Unexpectedly, erucamide is also quite effective, with oleamide of little value.

For many years, combinations of oleamide and stearamide have been used. It has been shown, however, that unless the ratios are controlled strictly, a softening eutectic will occur, resulting in worse results on blocking—increased tackiness—than if either additive was used alone.

Erucamide, when used by itself, provides both desired properties, has better temperature stability, and removes the margin of error.

The additives, when they migrate to the surface, are, in effect, keeping two layers of film apart. Blocking, therefore, would be related in part to the hardness of the amide's crystalline structure. This also is related to hardness at various temperatures. More blocking problems occur in

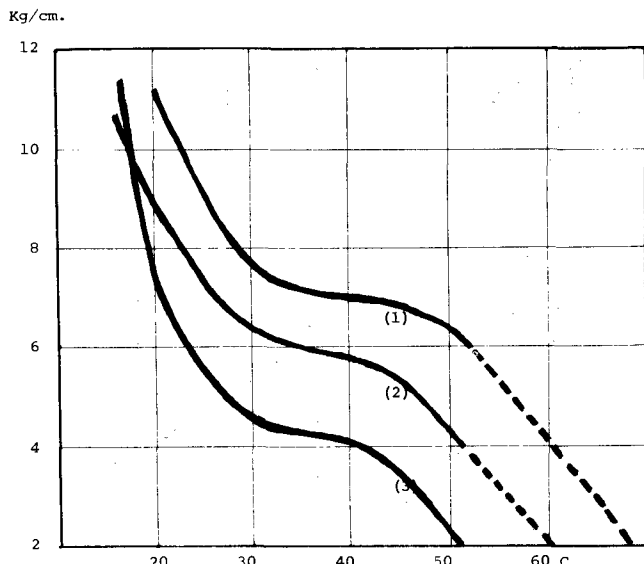


FIG. 3. Hardness vs. temperature (C) for pure erucamide (1), commercial erucamide (2), and commercial oleamide (3). See text for details of hardness measurement.

warm weather. This study, illustrated in Figure 3, shows that at room temperature, oleamide, a commercial erucamide (95%), and a purified erucamide (99%) all have ca. the same hardness. At 50 C or 120 F, which is the conditioning temperature used for induced blocking tests, purified erucamide is twice as hard as some of the commercial erucamides and four times as hard as oleamide.

Taking the preceding work into account, the purity of the erucamide takes on considerable significance. As production capacity for low density polyethylene in the U.S. in 1972 was 5.9 billion lb resin, more than half of which goes into film, the additional variables are certainly important. The impurities may be unreacted erucic acid, methyl ester, and nitrile formed during the synthesis.

Two series of tests were run on our material, as well as on others available. Hardness of the various erucamides was determined by melting samples in an aluminum pan, stirring the melt to obtain homogeneity, then allowing the samples to cool slowly into a cookie. A penetrometer was used, and the total depth of penetration under a load was measured. Values were calculated to obtain the hardness number according to the following formula:

$$H = \frac{L}{2 \pi R h}$$

where H = hardness number, L = the applied load, R = radius of the point, and h = depth of penetration in cm.

Samples of these erucamides then were incorporated into polyethylene film at 700 ppm. Film samples were cut to a size of 3 x 6 in. Ten pairs of film of the same type were conditioned in an oven at 48 C under a load of 1 psi for 24 hr and left at room temperature for 24 hr. Blocking then was measured, as the load required to separate one layer of film from the other.

Figure 4 shows that the hardness and blocking have a direct relationship, which also corresponds to the analysis (sample A 99%, sample B 97%, and sample C 95%, sample D had 3.5% methyl ester added).

During this test series, levels of slip also were determined, but the difference among the samples was insignificant.

As to heat stability, the difference in mp between oleamide and erucamide is not too significant. A typical mp of commercially pure oleamide is 72-74 C, while the mp of commercially pure erucamide is 78-83 C. Erucamide withstands a temperature of 380 F (193 C) for a period of 75

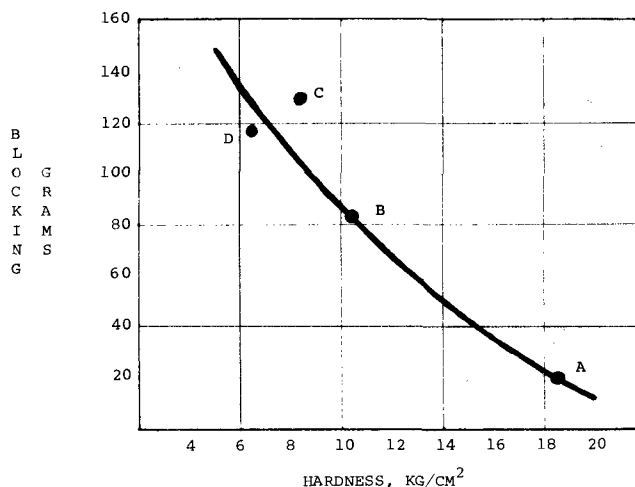


FIG. 4. Hardness and antiblocking effectiveness of erucamide samples of varying purity. Sample A = 97%, sample B = 97%, sample C = 95%, sample D = 3.5% methyl erucate added.

min in polyvinyl films, for example, without plating out; and the film remains clear, with an attractive gloss after four months of shelf testing.

In polyethylene also, it is the product of choice, because it is able to withstand relatively high processing temperature and simultaneously imparts excellent slip and improved antiblock characteristics. It can be used effectively in lamination of polyethylene to cellophane and polyethylene extrusion coatings. The recommended concentration in polypropylene sheets is 0.1%, for injection molding 0.15-0.25%, and it may impart antistatic properties at concentrations not exceeding 0.2%.

Further to relative heat stability, oleamide distills in the neighborhood of 170-175 C at 2-3 mm pressure, whereas erucamide distills at ca. 200 C at 0.3 mm pressure. This is significant and ensures against boiling out in the processing temperature of polypropylene and some polyethylene formulations.

There is an interesting derivative of erucamide, namely, N-stearyl erucamide. This product is known as high temperature slip agent no. 3 (HTSA 3 of Fine Organics, Inc., Lodi, N.J.). It is designed to impart slip, antiblock and mold release for normal and high temperature processing. The product is approved by the U.S. Food and Drug Administration for use in polymeric resins that may come in contact with food and food products when used in accordance with good manufacturing practice. Some of the processing takes place at high temperatures.

The boiling point of HTSA 3 is 440 C (824 F). It can easily withstand processing temperatures exceeding 316 C (600 F) without volatilization, darkening, or odor formation. Slip additives with poorer heat stability often boil out, and precise slip levels cannot easily be achieved.

The material is effective in a variety of thermoplastic resins, such as cellulose, polyolefins, polyvinyl polymers, polyvinyl copolymers, and polyamides, effective concentration levels being from 0.05-0.4%. It can be incorporated into high clarity thermoplastic film without impairment of the optical properties. In addition, films subjected to high humidity environmental tests remained clear, and there was no evidence of slip additive plate out.

#### ACKNOWLEDGMENTS

H.H. Lutzmann, P.D. Frayer, and P.E. Barth participated in some of the studies in this paper.

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[Received June 6, 1973]