Meadowfoam Monoenoic Fatty Acid Amides as Slip and Antiblock Agents in Polyolefin Film*

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SYNOPSIS

Mixed monounsaturated amides (MMA) of fatty acids from meadowfoam (*Limnanthes alba*) were effective slip and antiblocking agents for polyethylene films. MMA may compete with extant amides as additives for manufacture of PE films if their selling price is competitive. The MMA (79% *cis*-5-eicosenoic acid amides, 17% *cis*-5-, and *cis*-13-docosenoic acid amides, and 1% *cis*-5,*cis*-13-docosadienoic acid amide) required > 500 ppm but < 1000 ppm dosage to achieve high slip (coefficient of friction < 0.2) within 10 minutes of film blowing. For comparison, erucamide required < 250 ppm, oleamide required < 500 ppm, and stearamide required > 1000 ppm to give high slip levels within 10 min. Maximum antiblocking effectiveness of MMA, which developed at 1000 ppm, was equivalent to stearamide at 1000 ppm. © 1993 John Wiley & Sons, Inc.[§]

INTRODUCTION

Primary fatty amides are preferred slip agents added at approximately 0.1% levels in the production of low-density polyethylene (PE) film materials (U.S. PE film production was 6.3 billion lb in 1991).[1] They are less frequently used as antiblock and mold release agents in the manufacture of other flexible and rigid plastic products. Erucamide (EA), oleamide (OA), and stearamide (SA) are very cost effective for these applications and are widely used. However, other saturated and unsaturated amides with a chain length of 18–22 carbon atoms may be equally effective. Recently, Burg and Kleiman described the preparation of mixed meadowfoam fatty amides (MMA) and suggested their potential utility as slip and antiblock agents.[2]

Meadowfoam (*Limnanthes*) is a herbaceous flowering annual plant native to parts of the west coast of the United States and Canada. It is grown commercially as a winter–spring crop in the Willamette Valley of Oregon. Meadowfoam oil contains more than 95% C_{20} and C_{22} fatty acids, which are high in monoenoic unsaturation. A representative example of the fatty acid content of oil from *Limnanthes alba* reported by Chang and Rothfus contained 60% *cis*-5-eicosenoic acid, 17% *cis*-5- and *cis*-13-docosenoic acid, and 19% *cis*-5 and *cis*-13-docosadienoic acid.[3] Our interest in meadowfoam fatty acids and their derivatives stems from the need for crops that can replace those, such as corn and wheat, that are produced in excess of current market requirements.

Slip agents are additives that facilitate free movement of adjacent plastic sheets in sliding contact, often by causing microscopic surface roughness. Antiblock agents inhibit sticking (welding) of plastics to each other on contact or under moderate pressure. Properties that control the effectiveness of amides as slip and antiblock agents have been related to their mode of action.[4,5] Amides dispersed in melted PE at levels exceeding their solubility at

* The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

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room temperature migrate to the PE's surface during and after the blowing of films. Exuded amides form random aggregates on the film's surfaces that reduce intimate contact and cohesion between adjacent sheets. Slip or antiblock activity increases with increasing amounts of amide on PE surfaces until a critical level is reached. Thereafter, further increases in the amount of amide on the surface do not improve properties and may produce an undesirable oily layer on the film. The most effective amides are solids at room temperature, which may form crystals on the film surface, and diffuse rapidly from the PE.

For most applications, rapid development of slip is essential. Diffusion of fatty acid amides and development of a given slip level is faster for those having lower molecular weights and increased unsaturation. Rapidity of development of slip is also influenced by the dose level of amide in the formulation. Increasing levels of addition of an active agent produce higher surface concentrations of fatty amide in a given time. A related effect is the increased effectiveness of slip agent as the PE film thickness is increased. Thicker films, because of their greater volume/surface area ratio, produce a greater surface density of amide at a given dose level than do thinner films.

Fatty amides used in PE production include EA (*cis*-13-docosenoic acid, amide), behenamide (docosenoic acid, amide), OA, and SA.[4] Unsaturated amides, such as EA and OA, provide superior slip properties, whereas saturated amides, such as behenamide and SA, provide acceptable slip and superior antiblocking. EA displaced OA as the preferred slip agent for polyolefin film because it melts at a higher temperature and is more stable at extrusion temperatures. Use of EA for slip and antiblock agents was reviewed by Molnar.[6] SA also provides useful slip properties, although it is slower acting and has antiblock properties superior to those of EA and OA.

Fatty amides are easily prepared by reaction of fatty acids or fatty acid esters with ammonia at elevated temperature and pressure. Preparations and applications of fatty amides were reviewed by McKenna.[7] Recently, Burg and Kleiman reported a facile process for producing a mixture of *cis*-5-docosadienoic, *cis*-13-docosadienoic, and *cis*-5-eicosenoic amides from meadowfoam mixed fatty acids.[2] Only about 1% diunsaturated amides were included in the product. We have compared slip and antiblock properties of these mixed meadowfoam monoenoic primary fatty amides with those of commercial EA, OA, and SA slip agents and the results will be given in this article.

EXPERIMENTAL

Materials

Blown-film-grade low-density polyethylene (LDPE) was Norchem 3404 from USI (melt flow rate, 1.8 g/10 min, and density, 0.92 g/cc). EA (Kemamid E) and OA (Kemamid U) were from Humko Chemical Division, Witco Corp. SA (Armoslip 18) was from Akzo Chemie America. MMA were prepared by action of NH_3 on meadowfoam fatty acids in a xylene solution according to the method of Fore and Sumrell.[8] They were purified by vacuum distillation to remove xylene, followed by recrystallization of the amides from hexane as described by Burg and Kleiman.[2] The melting point was 76°C. Gas chromatographic analysis indicated that the MMA contained about 79% *cis*-5-eicosenoic acid amide, 17% *cis*-5- and *cis*-13-docosenoic acid amides, and 1% *cis*-5 and *cis*-13-docosadienoic acid amide.

Equipment

Films were compounded in a C.W. Brabender extruder (15 : 1 L/D barrel, 1.9 cm diameter, two heating zones) fitted with standard C.W. Brabender accessories. A two-zone mixing screw and a die with 17 1.6 mm-diameter holes were used when blending slip agents into LDPE. Films were blown from a 2.5 cm blown film die on a Brabender extruder (25 : 1 L/D barrel, 1.9 cm diameter, three heating zones, 5 : 1 compression screw). Film was uniformly drawn and wound on a takeup tower to minimize differences in film thickness. The coefficient of friction (CoF) and blocking were measured with a Model 4201 Instron Universal Testing Machine fitted with shop-made test jigs.

Formulation

Each amide was compounded with LDPE at levels of 250, 500, 1000, 1500, and 2000 ppm. To assure accurate dosage, amide was weighed onto a film of 3404 LDPE, wrapped in the film, and dropped into a stream of 500 g of LDPE pellets entering the screw of the extruder. Strands of LDPE–amide formulations were chopped into pellets, blended, and reextruded three times to mix the amides thoroughly. Extruder speed was 120 rpm and zone temperatures (from feed zone to die) were 135 and 140°C.

Film Blowing

Formulated pellets were blown into films with a 12.7 cm lay-flat and 7.66 : 1 longitudinal draw. Extruder zone temperatures (from feed zone to die) were 121, 130, and 136°C and die temperature was 140°C. Blown film was collected after torque and pressure levels became stabilized, which suggested that the level of slip agent in contact with the extruder surface was constant.

Film Testing

Films were tested for kinetic CoF according to ASTM D 1894 with an apparatus configured as in Figure 1(c) of the ASTM method. In this test, a foam-covered steel sled is wrapped with a section of the test film and dragged across a smooth table covered with another section of the test film. Force exerted in moving the sled at 150 mm/min is measured. Friction was measured at 10 min, 1 h, 24 h, 168 h, and 336 h. Each sample was cut and mounted with care so that the test areas were not disturbed by contact with hands or other surfaces. Blocking was tested according to ASTM D 1893 on samples consisting of two sheets that had been pressed together at 110°C for 4 h under a load of 1034 Pa. Samples were conditioned and stored at 50% relative humidity and 23°C. Results reported are averages from five measurements. Film thickness was 0.0393 mm with standard deviation of 0.0006 mm.

RESULTS AND DISCUSSION

All samples, except the control PE, developed low CoFs within the 10 min required to blow and test the film (Figs. 1–4). A considerable variation in measured CoF is evidenced by sharp breaks in the trend of some lines. Thinner than average films did not correlate with unusually high CoF values. CoFs decreased with time until the critical surface coating level was achieved. The minimum amount of slip agent required to produce the critical level was between 250 and 500 ppm for MMA, EA, and OA. Their minimum CoFs were (amide, CoF): MMA, 0.06; EA, 0.02; and OA, 0.02. SA required 1500 ppm to achieve its minimum CoF of 0.05.

One criterium for comparing the effectiveness of slip agents was the minimum dosage required to produce high slip (CoF < 0.2) within 10 min of extrusion. High slip was achieved within 10 min at the minimum dosage level (250 ppm) with EA (Fig. 1). OA required 10 min or less at a 500 ppm dosage level (Fig. 2). MMA required dosages greater than 500 ppm to reliably develop high slip within 10 min (Fig. 3). SA assured high slip within 10 min only at dosages exceeding 1000 ppm (Fig. 4). More rapid development of slip by EA than by OA was unexpected. The two amides have the same basic structure but EA's higher molecular weight should have slowed

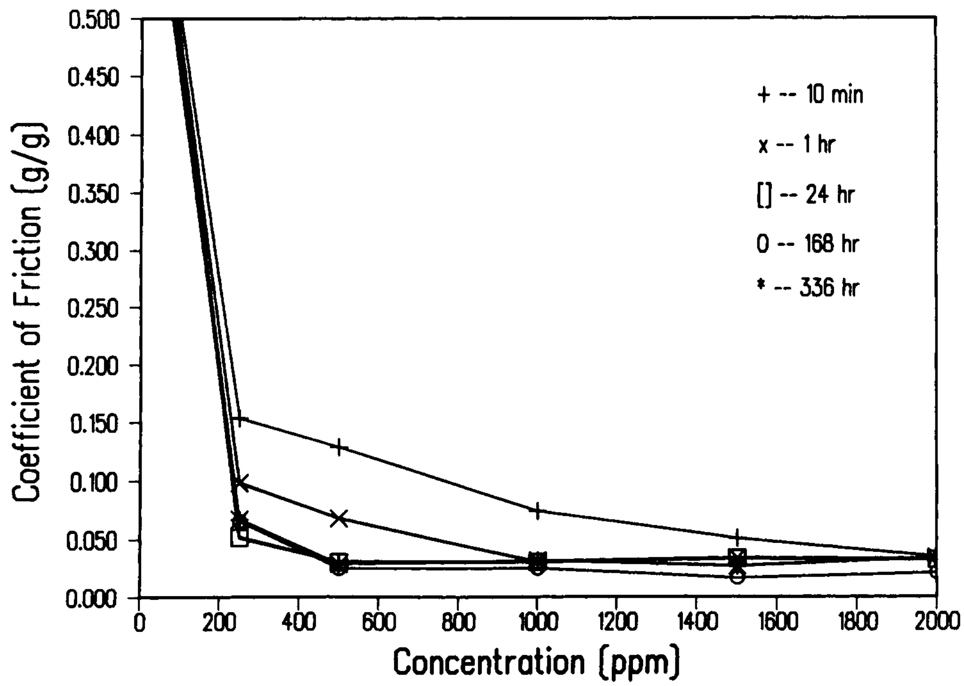

Figure 1 Coefficient of friction vs. concentration of EA.

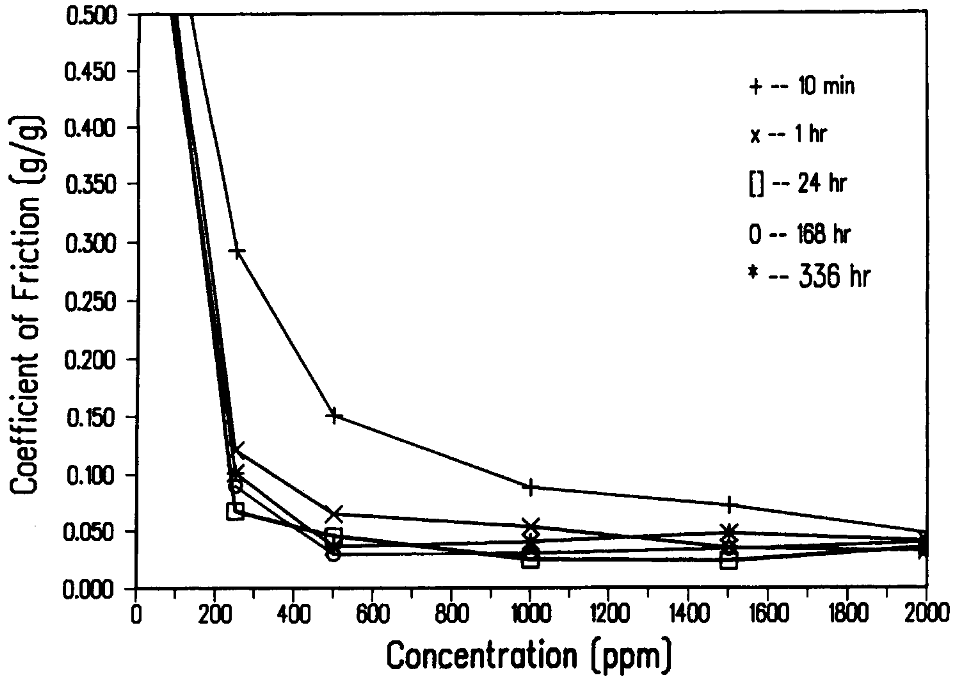

Figure 2 Coefficient of friction vs. concentration of OA.

its diffusion. Thompson reported a slightly more rapid development of slip by OA, but her example is flawed by the comparison of samples in which the molar concentration of OA is 34% greater than that of EA.[5]

Critical levels of amides for maximum antiblocking effectiveness were determined at 3 months (Fig. 5). EA and MMA reached maximum effectiveness at 1000 ppm, whereas OA and SA gave continually lower resistance to sheet separation up to 2000 ppm,

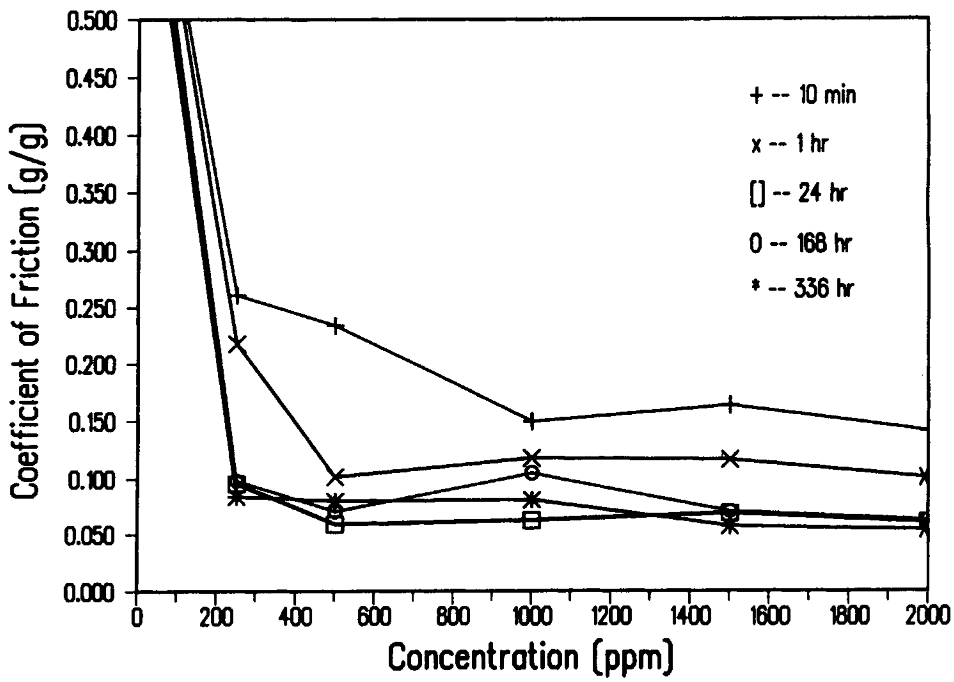

Figure 3 Coefficient of friction vs. concentration of MMA.

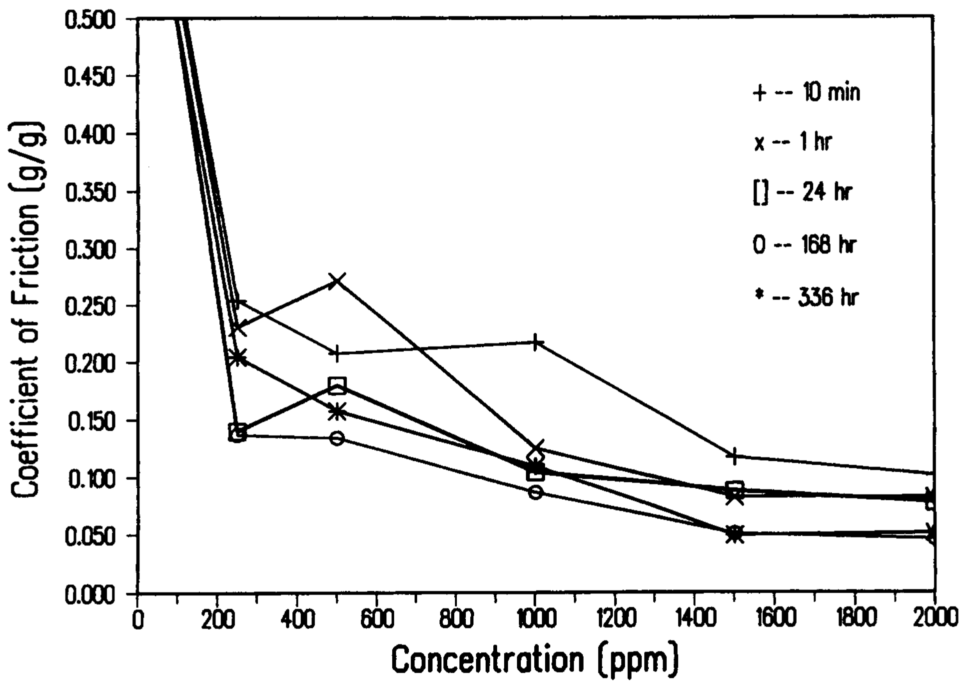

Figure 4 Coefficient of friction vs. concentration of SA.

our maximum loading. Parting effort was about 0.002 g/mm for EA and SA at 2000 ppm dosage, but increased to about 0.01 g/mm for MMA and OA.

MMAs were expected to lie between EA and OA in effectiveness. They are unsaturated, have an average molecular weight (315) closer to that of EA (335) than to that of OA (275), and have a melting

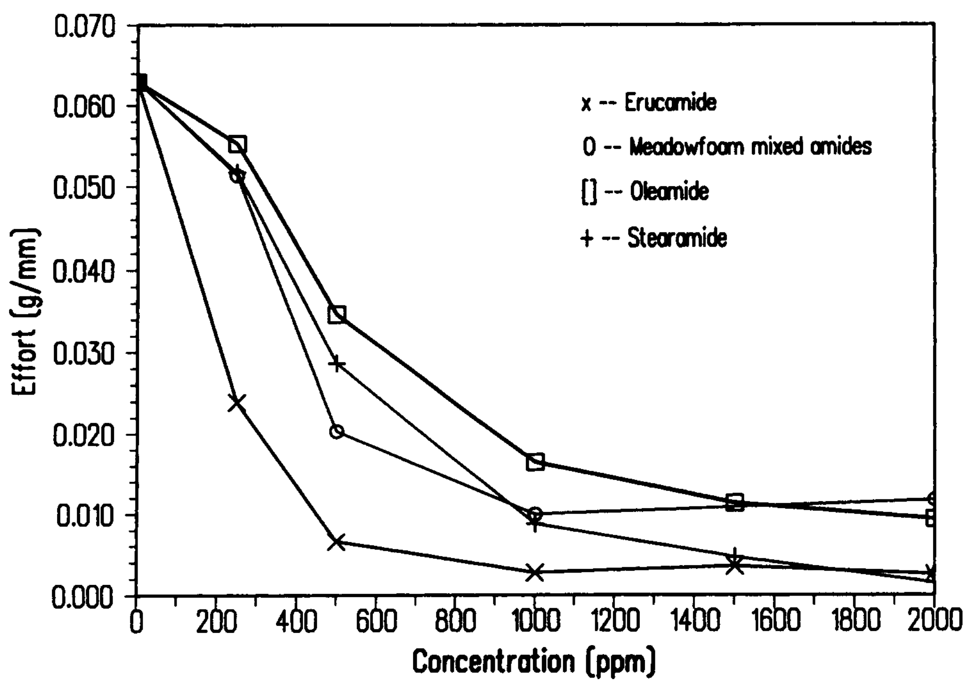

Figure 5 Blocking vs. concentration for EA, OA, MMA, and SA. Samples were tested 3 months after film was blown.

range (74–76°C) between those of EA (76–86°C) and OA (66–77°C). Saturated fatty amides such as SA (molecular weight 278 and melting range 98–108°C) are known to confer slip and antiblock properties more slowly than do unsaturated amides of comparable molecular weight.

CONCLUSIONS

The MMAs possess slip and antiblock activities comparable to those of amides currently on the market. Slight differences between MMA's properties and those of EA, OA, and SA could provide PE formulaters with means to tailor their products to more exactly fulfill specialized needs of their customers. MMA should be salable, if available in sufficient quantities at a reasonable price.

Mr. Kevin Callear prepared the meadowfoam fatty amides, Mr. Richard Westhoff compounded and blew the polyethylene films, and Mr. Gary Grose measured blocking and coefficients of friction.

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