large exchangers to pick up heat from distilled products leaving the unit. The crude oil contains many types of contaminants such as water, dirt, wax, sulfur and polymers. These materials tend to stick to the surfaces of the exchanger and eventually plug or restrict the flow and lower the efficiency which can be measured in terms of dollars from lost energy. These deposits also create differential heat spots which contribute to increased corrosion rates in the exchanger. The premature loss of the exchanger is a major expense; however, the most serious loss can be the downtime on a crude unit. Antifouling agents must have excellent detergent, dispersing and film-forming properties and function at high temperatures. Long-chain fatty amines and ethoxylated imidazolines are often used in these formulations which are injected continuously into the systems at very low dosages of 5-20 ppm.

Desalting

Crude oil arriving at a refinery has generally been treated to remove the bulk of water but it may contain up to 1.0% of water and salt. This salt is removed by mixing the crude with fresh water to extract the salt. The tight emulsions that are formed must be broken so that the crude is freed of the salt bearing water. A strong electrical field is applied to the crude to break these emulsions but a chemical demulsifier is generally used to enhance the demulsification process. The advantages of using these desalting compounds are: less salt and other water-soluble contaminants in the crude, better desalter performance due to a decreased emulsion interface and effluent water nearly free of hydrocarbon. Oleochemicals are sometimes used as a part of the demulsifier formulations.

Demulsifying

Hydrocarbons and water are in intimate contact throughout most of the refining process; desalting of crude, steam distillation and water washing of treated product are just some of the possibilities to form emulsions. The skimming of water, draining of tanks and other operations result in the accumulation of large quantities of emulsified oils. Although not a large consumer of demulsifying chemicals, there is a requirement in the refinery for a tank type treatment of oil for demulsification. By far the largest requirement for a demulsifier in the refinery is to obtain clean separations of water and hydrocarbons in the receivers after distillation. In application a chemical which functions both as an inhibitor and/or antifoulant and demulsifier is desired. Long-chain amine derivatives and fatty acid triethanolamine condensates are effective for this purpose.

Corrosion Protection

Fatty amines, imidazolines and amino amides are used in the overhead of distillation columns to reduce corrosion. Along with pH control to neutralize HCl formed, these inhibitors form films which protect the metal surfaces especially at the vapor condensation point.

Total market in the refineries of oleochemicals is estimated to be in excess of $125 million. The US market for transportation systems additives is $50-60 million. Oleochemicals capture ca. 25% of these markets.

TERTIARY RECOVERY

Finally, there is a very large potential market for oleochemicals that will develop when present, mostly experimental, enhanced oil recovery (EOR) projects are converted into full-blown standard practice. In a Bartlesville Energy Technology Center report of "Chemicals for Enhanced Oil Recovery" published in April, 1981, estimates of fatty acid derived surfactants volumes that could be used in EOR projects would exceed the available supply capacities of all the sources of suitable fatty acids. Simple soaps and ethoxylates of oleic acid are mentioned prominently. Extrapolation of some of the numbers presented indicate the potential market for oleochemicals in EOR could amount to over a billion dollars per year if it proceeds as outlined. How quickly the EOR market develops for oleochemicals and how large it actually becomes will be determined by the economics. Current markets are very small.

Marketing and Economics of Oleochemicals to the Plastics Industry

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ABSTRACT

The number of oleochemicals used in the plastics industry are many and varied. Usually the chemicals sold are designed for a specific application that depends on the end use and the economics of production. The percentage of oleochemicals that end up in the finished product is small, usually 0.1-1%, but it is there for a very important physical specification that the chemical imparts to the finished resin. The chemicals and applications are discussed by the structure of the additive and the property it imparts to the finished resin. The marketing of oleochemicals to the plastics industry usually requires considerable application and process research to develop specialized molecules that impart the desired properties to the finished resin. Market size and economics numbers refer only to the US markets.

SLIP AGENTS–FATTY AMIDES

Primary fatty amides of $C_{18\text{-}22}$ carbon atoms are the dominant slip agents used in polyethylene and polypropylene resins (1,2). The main compounds are either octadecenamide. The products function because, after the primary amides are dissolved in the resin, the polar group, on cooling, orients to the surface of the nonpolar resin which then forms a monomolecular film on the resin surface which allows the solid resin to be antiblocked or slip across an attached resin surface. The end result is the same as wax-coated or resin-coated papers which allow one resin surface to slide horizontally across another. An amide concentration of only 0.1-0.5% is used in plastic films. Since most of the polyolefin film is used in food wrap, the primary amides are approved under FDA Regulation 121.2509.

The simple amides used in this application are produced by the reaction of fatty acids or esters with anhydrous ammonia under pressure (3), according to the following equation.

$$RCO_2H + NH_3 \longrightarrow RCONH_2 + H_2O$$

In a batch process, the ammonia and acid react at ca. 200 C at a slight pressure (345-690 kPa) for 10-12 hr. Ammonia and water are continuously vented to facilitate completion of the reaction. A continuous process (4) has been patented, but has never been put into operation.

The main feedstocks used for the primary amide slip agents are oleic acid and erucic acid. The oleic used is high grade produced by solvent crystallization and distillation, and the erucic feedstock is prepared by the fractionation of esters or acids from rapeseed oil. Several forms of oleic and erucic amides are sold. They may be flakes, pellets or powders. Since the color and heat stability of the amides are important, they frequently will be distilled under high vacuum to maintain the quality of the final product. Besides the oleic and erucic derivatives, a small amount of stearamide is used in this application.

Properties and prices of commercially available primary fatty amides are shown in Table I.

Economics of production depend on the price of the feedstock followed by the rather large process costs of fractionation, amide production, purification of the amide and conversion of the amide to a particular physical form, e.g., flake, pellet or powder. Very few users purchase these products in bulk or even drums. The US market for primary amides for slip agents is 5 million lb each of octadeceneamide and docoseneamide and 1.5 million lb of octadecanamide for a total of 11.5 million lb.

TABLE I

Primary Fatty Amides

Product	Melting point (C)	Price ($/kg)
Dodecanamide	103	N/A
Tetradecanamide	104	N/A
Hexadecanamide	108	N/A
Octadecanamide	109	2.68
Octadecenamide	70	3.12
Docosenamide	85	5.17

LUBRICANTS, MOLD RELEASE AGENTS–FATTY AMIDES

Fatty amides are used as internal and external lubricants for a variety of resins. The main resins are polystyrene, ABS, PVC, polyolefins, polyvinylacetate and phenolic resins. Besides the primary amides mentioned in the previous section, difunctional amides such as ethylene (5) and methylene *bis*-amides (6) and secondary amides produced by the reaction of fatty acids with a fatty amine are also used. The following reactions describe the methods of production.

EBS–N,N'-ethylene *bis*-stearamide

$$2RCO_2H + H_2N(CH_2)_2NH_2 \xrightarrow{150\text{-}200\ C} RCONH(CH_2)_2NHCOR + 2H_2O$$

MBS–N,N'-methylene *bis*-stearamide

$$2RCONH_2 + CH_2O \xrightarrow[150\ C]{} RCONHCH_2NHCOR + H_2O$$

Secondary amides–stearyl stearamide

$$RCO_2H + RNH_2 \xrightarrow[150\text{-}200\ C]{} RCONHR \quad R = \text{Stearyl}$$

Table II shows some of the properties of these compounds.

These products are also available in different physical forms from bulk to flakes or powders. The form sold usually depends on the blending facilities available in the user's plant. The lubricants and/or mold release agents are classified as either internal or external. In either case, they should not be confused with spray-on mold release agents. The external lubricant's function is to effect release of polymer melts from the metal surfaces of processing equipment. Internal lubricants are considered to be soluble in the polymers; therefore, they will reduce the cohesive forces of the polymer and promote polymer flow.

The economics of producing amide-type lubricants depends on the source of the acids used in the production of these materials. Obviously companies basic in fatty acids should have a cost advantage. Table II also lists the volume and prices of various amides.

FATTY ACIDS, SALTS, ESTERS AND KETONES–LUBRICANTS, MOLD RELEASE AGENTS

Other oleo-derived chemicals are also used as lubricants for the plastics industry. The main resins used for these lubricants, both internal and external, are ABS, polystyrene, polyolefins, PVC, phenolics and melamines. The fatty acids used are usually stearic, either the hard tallow type or fractionated, to obtain a higher melting point, better color and better heat stability. The estimated usage is 15 million lb at a price of ca. \$0.98/kg. Again, the acids may be used in bulk or in a special physical form, such as flake or powder.

By far the largest use of fat-derived lubricants in the plastic industry is in the form of metallic stearates. Table III shows the products, volumes and approximate prices.

The metallic stearates are usually sold in powdered form and improved products are always being developed. One of

TABLE II

Difunctional Fatty Amides

Product	Melting range (C)	Volume (million lb)	Flash point 0 C, CC	Typical color, Gardner	Price ($/kg)
EBS Ethylene *bis*-stearamide	140-145	10.5	304	3	1.32
MBS Methylene *bis*-stearamide	135-140	>1.0	260	5	2.00
SS Stearyl stearamide	92-95	>1.0	246	4	5.00
OS Oleyl stearamide	70-75	–	260	3	

TABLE III

Metallic Stearates

Product	Volume (million lb)	Price ($/kg)
Calcium stearate	37.0	1.72
Zinc stearate	19.0	1.89
Magnesium stearate	5.0	1.83
Aluminum stearate	0.2	2.05
Others	0.25	2.37
Total	61.45	

the drawbacks to stearates is the high dusting properties that are apparent on addition to the resin. Improvements in processing to produce a material with higher density has aided in alleviating this problem.

The esters used as lubricants in the plastics industry generally fall into three classes:

- Alcohol esters formed by the reaction of standard primary alcohols with fatty acids. A typical example would be stearyl stearate. Generally speaking, the higher the molecular weight of the ester, the less the internal lubricating effects will be imparted to the resin.
- Polyhydric esters formed by the reaction of a fatty acid with a polyol such as glycerine. A typical product would be glycerol monostearate. The lower the ester number, the more internal lubrication is obtained in the resin. Another important, but low volume ester, is produced by the reaction of lauric acid with a polyoxyethylene glycol (MW 400) which is described as PEG 400.
- Long-chain esters formed by the reaction of fatty acids and alochols with chain length distributions higher than C_{18}. These esters are used in specialty cases where external lubricating properties are needed and they can be considered as high priced items.

Fatty ketones are produced by the reaction of fatty acids under high temperatures and the use of metallic oxide catalysts such as calcium oxide or magnesium oxide according to the following reaction:

$$2RCO_2H \xrightarrow{\text{catalyst}} RCOR + CO_2 + H_2O$$

The main ketone, which is produced in relatively small quantities, is stearone, diheptadecyl ketone. It is a specialized product and sells for ca. $3.30/kg.

PLASTICIZERS–STABILIZERS

The plasticizer usage in this market is quite substantial, amounting to ca. 2 billion lb per year. Of this total, ca. 10% can be classified as having part of the product derived from an oleochemical. The largest segment of this percentage is described as epoxy plasticizers, derived from natural triglyceride oils or esters of tall oil acids.

The epoxidation of soybean oil essentially adds an oxirane function to the unsaturated bonds of the hydrocarbon chain, producing a final product with a low iodine value (5-7) and a high oxirane content (7.0%).

Epoxidized products are primarily used in PVC resins where they act as plasticizers and heat and light stabilizers. They are also used in a variety of other resins. These compounds are often referred to as "epoxies" but they should not be confused with glycidyl ether epoxy resins. About 110 million lb of epoxidized soybean oil at a price of $1.23/kg and 40 million lb of epoxidized octyl tallate at $1.54/kg are used per year.

Two other oleochemical-derived plasticizers used in the resin industry are esters of sebacic acid and azelaic acid. Both of these dibasic acids are produced from natural oil by the following reactions:

Azelaic acid:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H + O_3 \xrightarrow{H_2O} CH_3(CH_2)_7CO_2H + HO_2C(CH_2)_7CO_2H$$

Sebacic acid:

$$CH_3(CH_2)_5\underset{\displaystyle OH}{CH}CH_2CH{=}CH(CH_2)_7CO_2H \xrightarrow{NaOH,\ \Delta} HO_2C(CH_2)_8CO_2H + CH_3(CH_2)COCH_3$$

The usual variety of alcohols will be used to produce the diesters, but the main alcohol usage will be 2-ethylhexanol because of economic reasons. For special applications higher molecular alcohols are used. About 15 million lb of azelates at $2.20/kg and 3 million lb of sebacates at $2.93/kg are used.

ANTISTATIC AGENTS

Introduction of plastic formulations into literally hundreds of applications in the past 50 years led to many observations that there is build-up of static charges on the surface of the resin due to the nonconductive natures of plastics. The charge build-up causes many problems, including sparking, discharge and accumulation of dust and dirt on the surface of the resin. This phenomenon has been alleviated by treating the resin, internally or externally, with fat-derived antistatic agents which allow for static charge decay.

External antistatic agents are usually applied by spraying or dipping a 0.1-1.0% solution in water or in an alcohol-water mixture. The advantage of incorporating some water in the solution is the immediate antistatic protection obtained as the hydrophilic antistatic agent retains some of the water which bleeds off accumulated charges. The external antistats are easily removed during subsequent operations so the static charge can rebuild in subsequent handling of the resins.

The most common externally used antistats are quaternary ammonium compounds or ethoxylated glycerol esters of fatty acids. The quaternary ammonium compounds are usually trimethylalkyl or *bis* (2-hydroxyethyl) alkyl ammonium halides and are sold in special formulations for specific uses. The price will range from $2.50 to $5.00/kg for the quaternary ammonium compounds, which then will be formulated into a specific formulation. The ethoxylated glycerol esters sell for $2.50-4.00/kg and again will be sold as a formulated product. The total market for the active ingredients is probably less than one million lb/year. The formulated products are often sold as specialty products for a very specific application with the prices ranging from $8.00/gal to as high as $300.00/gal (7). Modern Plastics estimates the volume of antistatic agents was at 2,800 metric tons for 1982.

Internal antistats are compounded into the resins during processing and will tend to bloom to the surface. Once present on the surface, the mechanism is the same as for externally applied antistats. The internal antistats are used at 0.1-4.0% and their effectiveness varies greatly from resin to resin. The bloom time also varies from a few hours to a few days before the expected antistatic protection is fully effective. Too high a level of antistat results in a

TABLE IV

Antistatic Agents

Product	Activity (%)	Use	Price ($/kg)
bis (2-Hydroxyethyl)tallow amine	100	HDPE	3.52
bis (2-Hydroxyethyl)coco amine	100	PP,ABS styrene, SAN	5.25
bis (2-Hydroxyethyl)stearyl amine	100	HDPE	6.60
bis (2-Hydroxyethyl)tallow amine + HDPE	75	HDPE	9.19
bis (2-Hydroxyethyl)tallow amine + LDPE	50	LDPE	8.38
bis (2-Hydroxyethyl)coco amine + SAN	50	ABS,SAN	7.35
bis (2-Hydroxyethyl)coco amine + PS	50	PS,ABS	6.73
Glycerol monostearate	100	LDPE	2.20
Glycerol monooleate	100	PO films	2.75

greasy surface with printing and labeling problems and no increase in antistatic behavior. The primary advantage of using internal antistats is that any antistat lost from the surface due to handling of the resin will be replaced by the remaining antistat in the bulk of the plastic.

The most common internal antistats are ethoxylated amines and glycerol esters that are added to the resin formulation as liquids, but recently a series of solid antistats have been developed that are easier to handle and disperse during molding operations. The ethoxylated amines are produced by adding 2 moles of ethylene oxide to a primary amine. The primary amine is usually a coco, tallow or octadecyl chain length.

$$\mathrm{RNH_2 + 2\underset{\backslash\;O\;/}{CH_2CH_2} \longrightarrow RN(CH_2CH_2OH)_2}$$

Recently, a series of solid antistats have been introduced which are patented (8) formulations in which 50-75% of the ethoxylated amines are concentrated into a resin which allows the antistat to be powdered, flaked or pelletized so that they can be added as a solid during compounding.

Table IV shows compositions and pricing for the various antistats now on the market. The total market for internal antistatic agents of this type is ca. 5 million lb/year.

FATTY ACID PEROXIDES–CATALYSTS

There is a small specialty market for two peroxides that are produced from fatty acids. The main product is dodecanoyl peroxide and the second is decanoyl peroxide. They are produced by the following reaction:

$$\mathrm{2RCOCl + Na_2O_2 \longrightarrow RCO_4R + 2NaCl}$$

The organic peroxides are a class of compounds of fundamental importance to the plastics industry. The fatty derived peroxides are not large commercially, but they do have specialty uses. The peroxides act as initiators for the synthesis by free radical polymerization of linear addition polymers such as PVC, polystyrene and LDPE. Their utility as initiators or curatives results from their capacity to decompose under suitable conditions into free radicals. Obviously the rate of catalyzation using different molecular weight fatty acids can be controlled because of the percentage of peroxide in the catalyst. The market for fatty peroxides is small, ca. 250 thousand lb per year and the selling price is $5.50/kg.

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