

HOW
ABOUT
THE
NEW
MARINE
OILS
?



UNITED STATES DEPARTMENT OF THE INTERIOR
FISH AND WILDLIFE SERVICE
BUREAU OF COMMERCIAL FISHERIES



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MARINE OILS — NEW AVENUES FOR VENTURE

Marine oils present the paint technologist with abundant opportunities for profitable use because of the unique properties and relatively low cost of marine oils. We answer three questions in the following discussion:

WHAT ARE MARINE OILS?

HOW ARE MARINE OILS PRODUCED?

HOW ARE MARINE OILS USED?

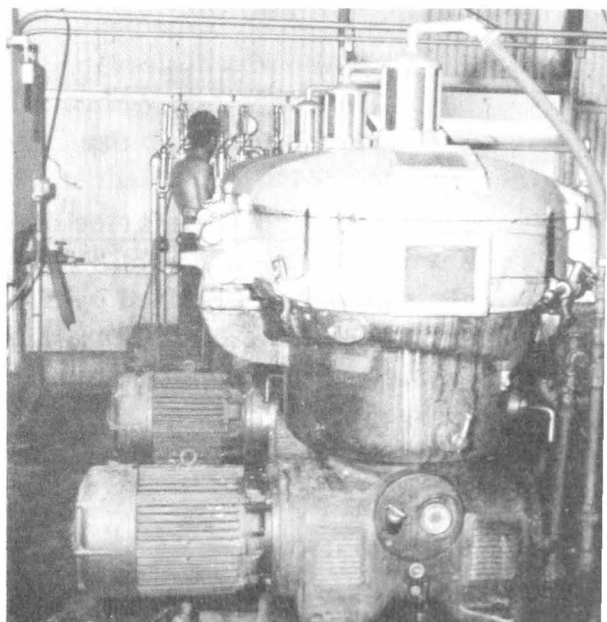
A few of the possibilities are shown in the answer to the last question.

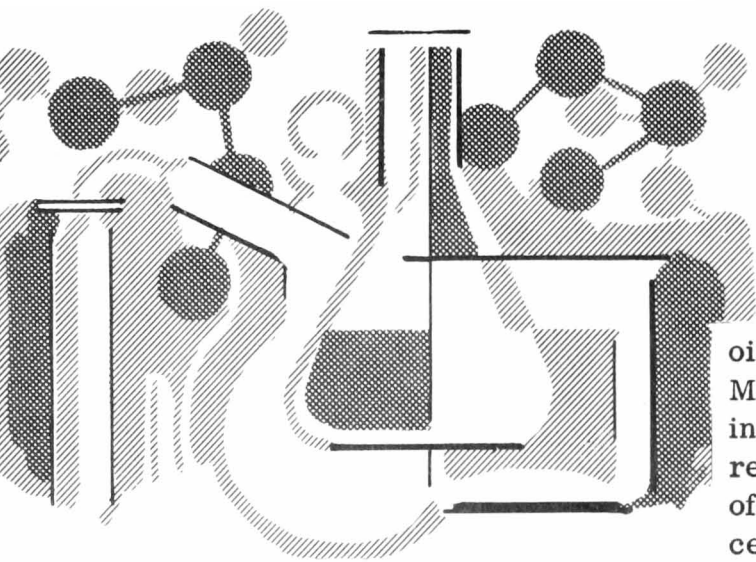
Marine oils are primarily mixtures of triglycerides. Marine oils are unique because the fatty acids in the triglycerides range in length from 14 to 24 carbon atoms with a high percentage of 4, 5, and 6 double bonds. This high degree of unsaturation in menhaden oil results in iodine values ranging from 150 to 190.

Marine oils are prepared from many varieties of marine fish and mammals. The average annual production during the past 10 years has been about 180 million pounds. Distribution was as follows: 78% from menhaden, 7.3% from herring, 5.1% from Pacific sardine, 3.1% from tuna and mackerel, and 6.5% from other sources, including whales and seals.* (From Bureau of Commercial Fisheries TL-14, F. B. Sanford and C. F. Lee.)

HOW ARE MARINE OILS PRODUCED?

Most crude marine oils are produced mainly by cooking the whole fatty fish, pressing the cooked mass to express freed oil and water, and centrifuging to separate the oil from the press liquor. The oil is generally given a hot-water rinse to remove water-soluble impurities and is polished by centrifuging to a clear oil. At this stage the

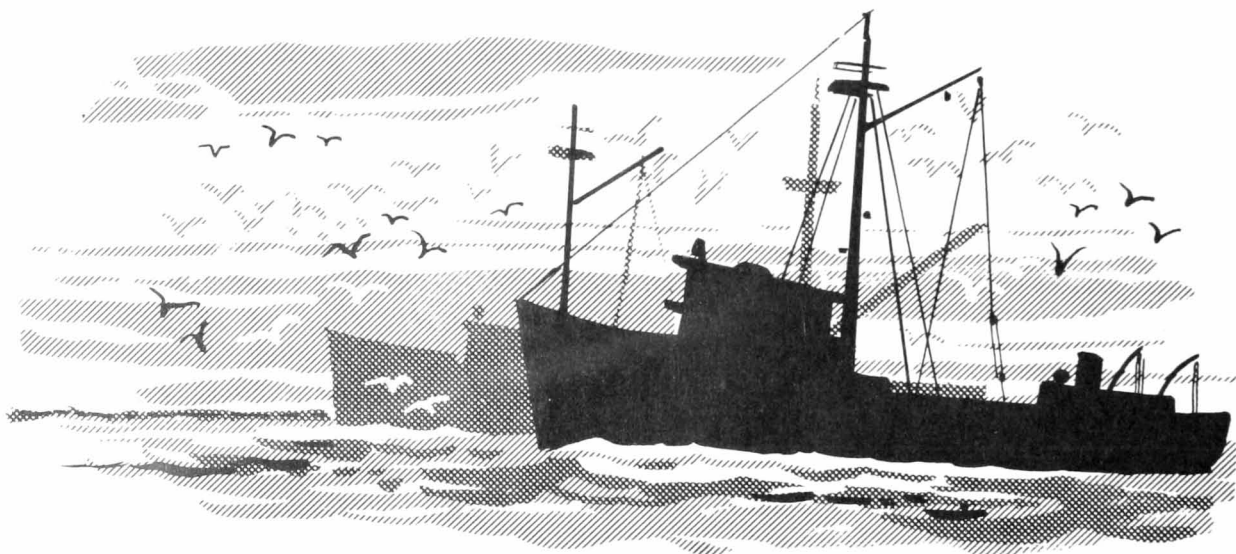




oil is ready for market as crude marine oil. Marine oils have been upgraded in quality in recent years by developments such as refrigerated boats for better preservation of the raw fish and improvements in processing techniques. Resulting oils have increased stability and uniformity, lower acid number, lighter color, and less odor.

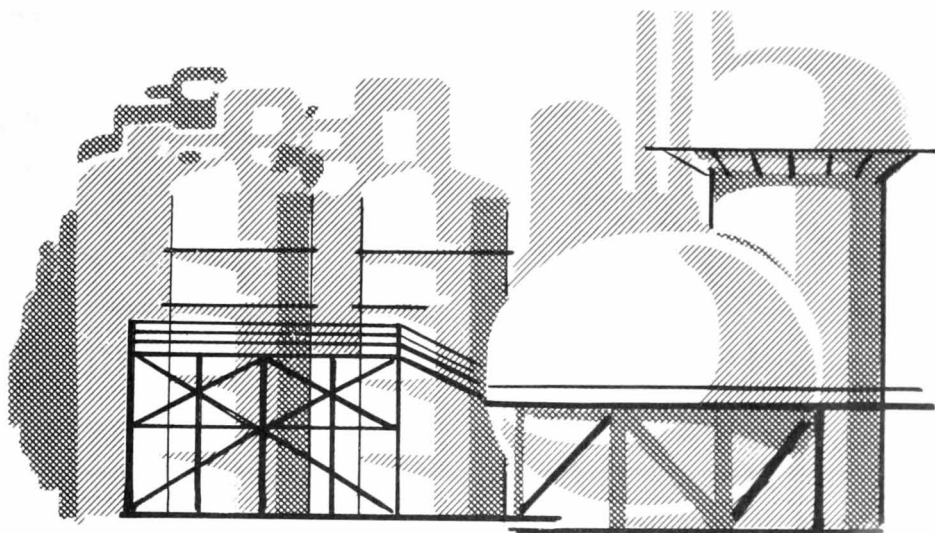
Alkali-refined marine oils are produced from the crude marine oils by using a caustic solution to neutralize free fatty acids present. The mixture is then centrifuged, washed, and clarified to a soap-free state. This process reduces free fatty acids to a very low level and removes much of the color and residual odor.

Refined and bleached marine oils are produced by clay bleaching the alkali-refined marine oils, which are thus lightened in color and made virtually odorless.



Light cold-pressed marine oils are produced by refrigerating crude marine oil to a temperature that solidifies the more saturated triglycerides. The solid triglycerides are removed by filtration, and the filtrate is marketed as light cold-pressed marine oil. Thus, light cold-pressing increases the iodine value and the drying qualities of the oil.

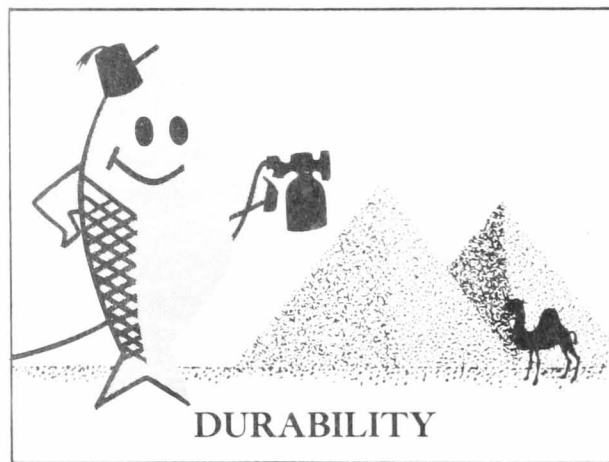
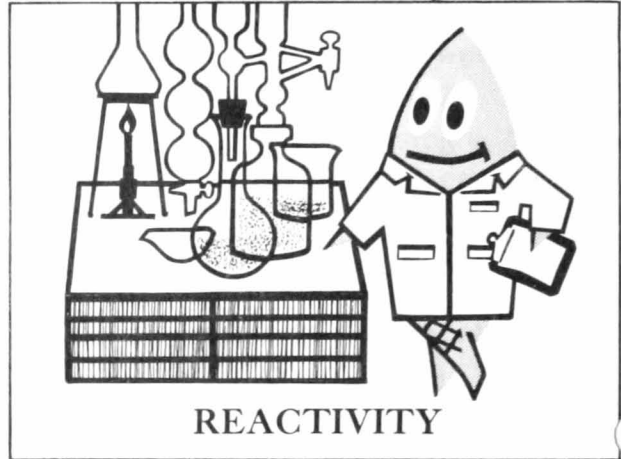
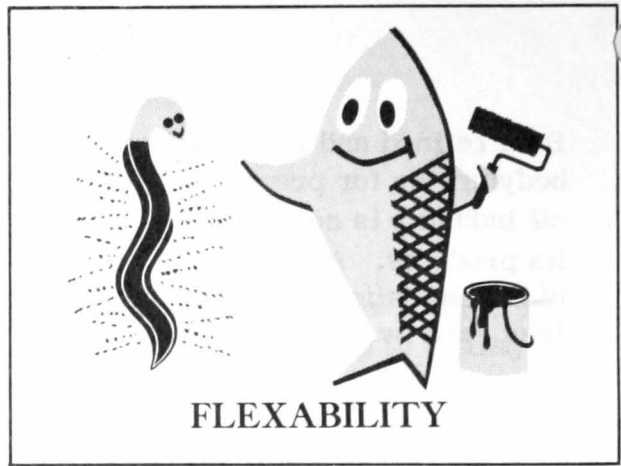
Both refined and light cold-pressed marine oils are suitable for blowing, for heat bodying, or for preparing synthetic resins for use in paint products. The marine oil industry is continually advancing in technology and seeking new ways to improve its products. A promising refinement presently in the pilot-plant stage is molecular distillation of marine oils. The resultant oils are almost colorless and odorless, and even quite bland to taste.

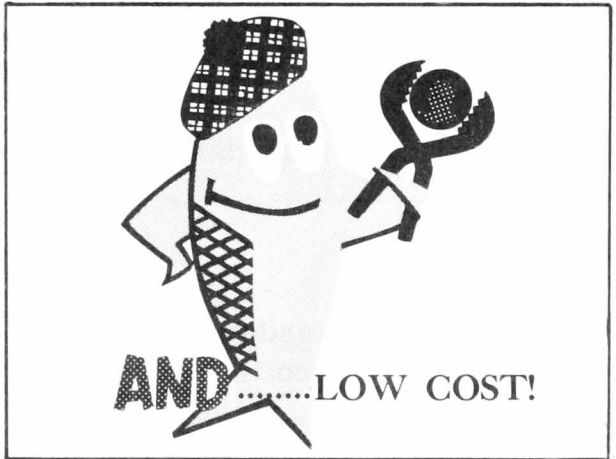
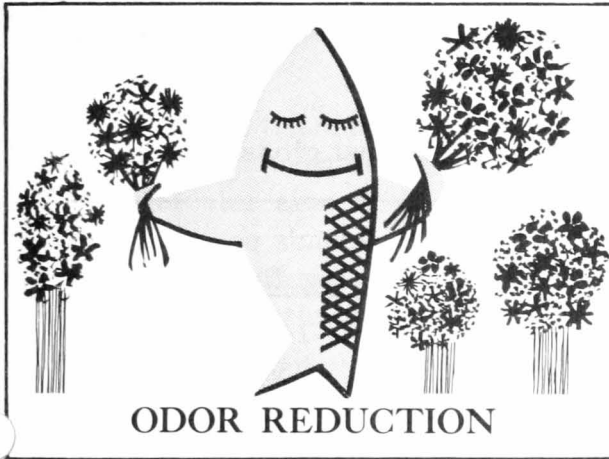
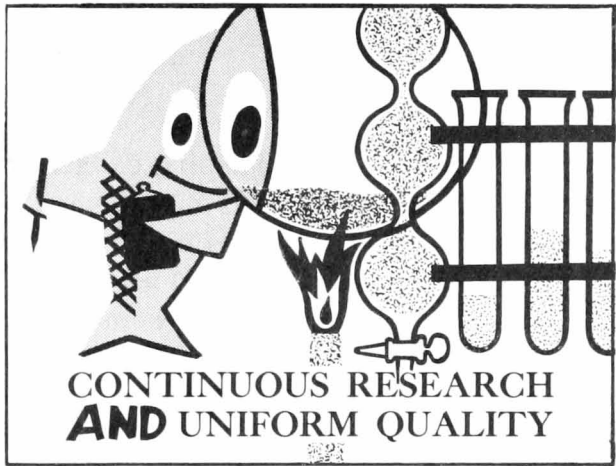
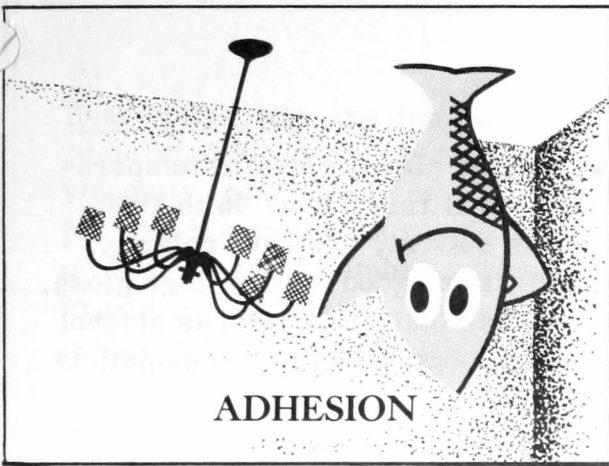


HOW ARE MARINE OILS USED?

Marine oils may be processed in many ways to produce valuable products for the paint industry. The following are several important applications reported to the Bureau by the industry.

Marine oil alkyds have advanced marine oils into what is probably the most versatile, durable, economical, and widely used class of film binders. Much progress is reported with dibasic acids, such as isophthalic, in the production of marine oil resins. These resins have minimized the problem of tack, yellowing, odor, and color, yet have retained the desirable characteristics of wettability, fast drying, high molecular weight, flexibility, and economy that are inherent in marine oils. The industry also reports the successful use of alkaline refined menhaden oil in a TT-R-266a Type I alkyd resin (23% phthalic anhydride, 60-65% fatty acids). A comparison of alkali-refined menhaden oil with linseed, soya, safflower, dehydrated castor oil, and tall oil (less than 1% rosin) will show the superior drying time, hardness, viscosity, and economy of the menhaden oil alkyd. The durability of such a marine oil alkyd will be as good as most and better than some of the other oil alkyds.





Dicyclopentadiene-treated marine oils are a major advance in upgrading the drying and the color stability of marine oils while maintaining many of the desirable characteristics of marine oils. Dicyclopentadiene treatment is a first major step to form synthetic copolymers from marine oils. These products are light in color and have extremely low acid numbers that extend their versatility into metallic paints. They are high in oil content, but they dry with almost no tack. Uses include aluminum paints, enamels, rust-inhibitive primers, flat paints, and varnishes.

Table 1. --Typical formula and characteristics for general purpose aluminum paint

<u>Materials</u>	<u>Pounds per 100 gallons paint</u>
Standard lining aluminum paste	150
Coumarone-indene, 60% in mineral spirits	63
Dicyclopentadiene-treated marine oil, Z6 viscosity	242
Mineral spirits	285
High-flash naphtha	46
Cobalt drier, 6%	2

Characteristics

- Weight per gallon - 7.9 pounds
- Leafting - Excellent
- Viscosity - Approximately 20 seconds #4 Ford cup

Blown oils are made by passing oxygen through marine oils at elevated temperatures. This process yields high viscosity products that range from 46 to 1066 poises (Z3 to Z10 Gardner-Holdt), reduce slowly in solvent, and have polarity. This treatment results in good adhesion, nonpenetration, good drying, high gloss, pigment wettability, and some compatibility with polar materials such as alcohol or water. After the oxidized oil film dries, it is no longer soluble or compatible with water and is a tough, durable, glossy coating.

Applications for an oil of this type include maintenance finishes, nitrocellulose plasticizers, barn and roof paints, cold cut enamels, rust-proofing compounds, anti-fouling paints, and low-cost finishes.

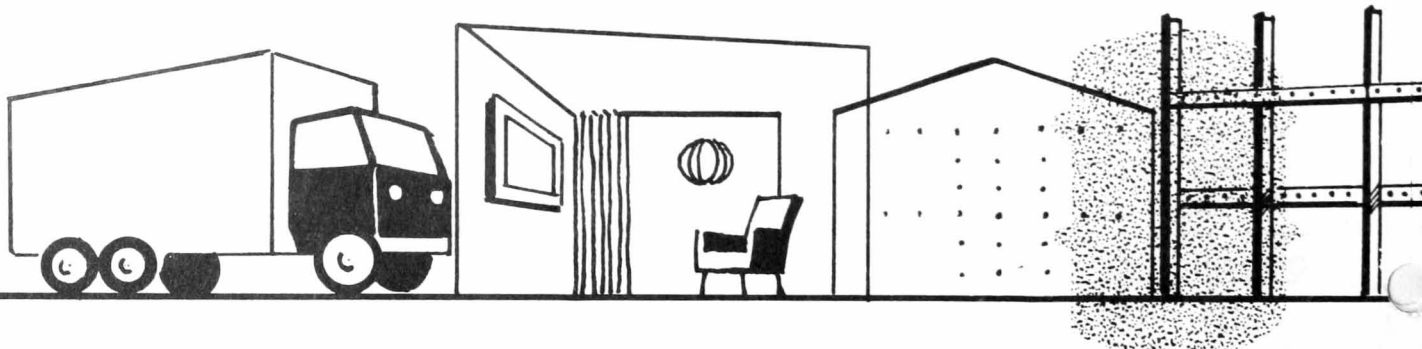
Table 2.-- Typical formula and characteristics for a low-cost gloss enamel

<u>Materials</u>	<u>Pounds per 100 gallons paint</u>
Persian Gulf red oxide	141
Calcium carbonate	238
Soya lecithin	2.5
65% N. V., Y viscosity tall oil rosin-gloss oil	222
75% N. V., Z3 viscosity, blown marine oil	128
Mineral spirits	91
Cobalt drier, 6%	1.33
Zirconium drier, 6%	1.25
Water	223

Characteristics

- Weight per gallon - 10.48 pounds
- Viscosity - 78-83 KU (Krebs Units)
- *Raw material cost - approximately 58 cents per gallon

*In this and in the following formulas, RMC (raw materials cost) is based on approximate prices in force during summer of 1961.



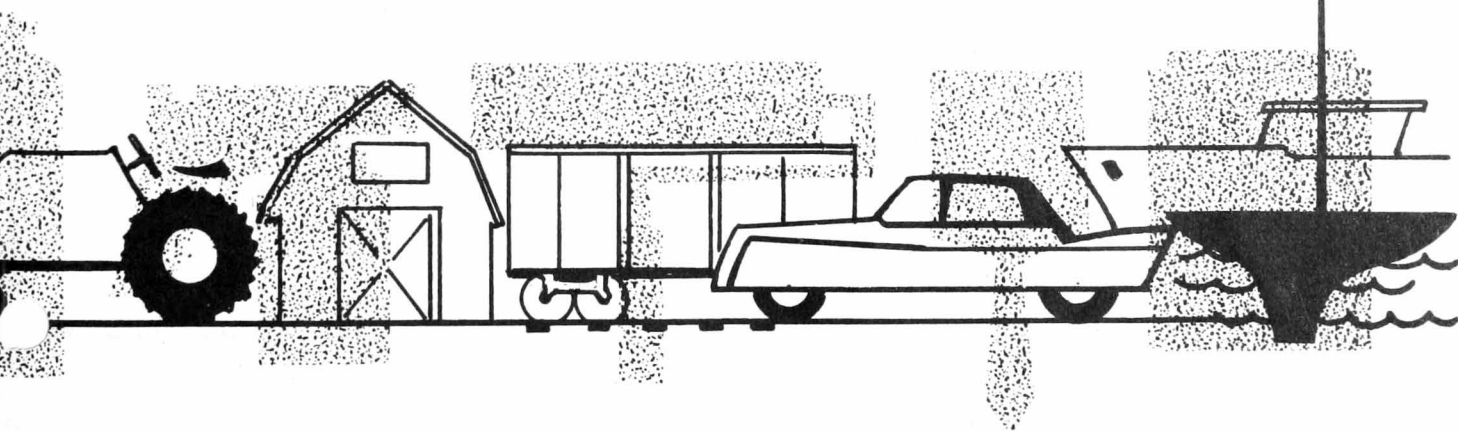
Heat-bodied oils are marine oils polymerized by high temperatures, which process removes the odor and results in a product with good color stability. They range in viscosity from 6 to 46 poises (V to Z3 viscosity, Gardner-Holdt). They are ideal for cold blending with resins to produce excellent leafing metallic finishes because of their low acid number. The characteristics of heat-bodied marine oils are easy brushing, toughness, elasticity, light color, and excellent durability. These oils compare favorably in durability with the higher priced linseed oils.

Table 3.--Typical formula and characteristics for high-quality exterior eggshell wood or masonry paint

<u>Materials</u>	<u>Pounds per 100 gallons paint</u>
Anatase titanium dioxide	144
Rutile non-chalking titanium dioxide	36
Acicular zinc oxide	200
Clay	240
Soya lecithin	5
Z2-Z3 kettled marine oil	320
Regular mineral spirits	197
High boiling mineral spirits	0.54
Cobalt drier, 6%	4.3
Calcium drier, 4%	4.0
Lead drier, 24%	6.7

Characteristics

Weight per gallon - 12.1 pounds
PVC (pigment volume concentration) - 34%
TNV (total non-volatiles) - 77.8%
Viscosity - 80-85 KU (Krebs Units)
NVV (non-volatile in vehicle) - 50%
RMC (raw material cost) - approximately \$1.41 per gallon



Double processed oils are marine oils that are heat bodied and subsequently blown. These oils are used where the unique features from both processes are desired. Their major use is in caulking and glazing compounds where light color, elasticity, excellent pigment wettability, and nonstaining are essential.

Table 4. -- Typical formula and characteristics for a good gun-grade caulk

<u>Materials</u>	<u>Pounds per 100 gallons paint</u>
Double-processed marine oil Z5-Z6 viscosity	175
Polybutene polymer	162
Soya fatty acids	15
Mineral spirits	57
Cobalt drier, 6%	3.8
Fibrous talc	245
Whiting	790
Anatase titanium dioxide	25

<u>Characteristics</u>
TNV (total non-volatile) - 96%
RMC (raw material cost) - 5 1/2 cents per pound

SO WHAT ?

Processed marine oils offer unique qualities that produce outstanding results in many products. Recent marine oil research has brought out products that formerly were believed impossible with this economical oil. Full understanding of marine oil properties translated to proper formulations result in their utilization in many products of superior quality.

When the manufacturer recognizes the many places where he can use marine oils, he will benefit from the high-quality products that can be formulated, the superior results achieved, and--all at reduced costs.

Industrial fire-retardant paints, epoxies, styrenated vehicles, polyurethanes, and other research developments should open up huge new avenues for ventures with marine oils.