having different retention characteristics. The same type of a semilogarithm plot is constructed for the second chromatogram, and it can be deduced to which homologous series the unknown belongs. If the point is resolved and appears on both lines, it can be assumed that the peak contains at least two components. For samples having only a few unknown components, it is possible to add knowns from two or three different homologous series and in this manner to construct identification plots.

Another advantage of the technique is the identification of very small sample peaks. The procedure has proved highly useful on chromatograms obtained with equipment using a β-ray detector where sufficient amounts of a sample cannot be obtained by condensing and trapping the effluent of the gas chromatogram for chemical or infrared analysis. Obviously the technique works best where high resolutions of components are obtained and where the equipment is sufficiently stable to give good, reproducible, retention volumes. Still another advantage is that the method works well on partially resolved peaks. After experience with the method had been acquired, coupled with a knowledge of the limitations of gas chromatography, chromatograms containing 20 or more components were resolved.

The method may also have application in liquid chromatography where good resolution and a linear relationship can be obtained between elution volumes and some chemical or physical property such as the molecular weight, degree of polymerization, or other noncolligative property.

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Continuous High Temperature Preparation of Alkylolamides

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Abstract

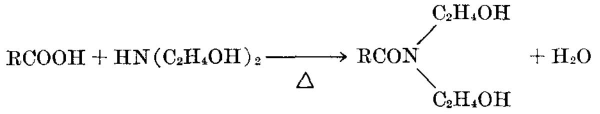
Lauric diethanolamide was prepared from methyl laurate and diethanolamine in the presence of an alkaline catalyst by a continuous high temperature process. The conventional batch process requires cycle times of 2–6 hr which can lead to undesirable by-products.

With a reaction time of about 10 sec, product purity of 91–94% was obtained at 149C for an absolute pressure range of 10–760 mm Hg. When reaction temperature was lowered to 110C, product purity became poorer as the absolute pressure was increased from 30 mm Hg to 760 mm Hg.

Two studies for optimum catalyst content of either KOH or sodium methylate showed that maximum product purity of about 97% was obtained at 0.20% catalyst by weight.

Alkylolamides are a widely used class of nonionic surface active agents, particularly fatty diethanolamides which are popular as foam builders for the alkyl aryl sulfonates. They are found in products ranging from laundry detergents to high-quality shampoos. The composition of alkylolamides can vary considerably, however, depending on the reactants employed.

One of the earliest commercial alkylolamides was the Kritchevsky detergent (1). For a typical product, one mole of coconut fatty acid was mixed with two moles of diethanolamine in a still. The mixture was heated to about 150–170C, and water was slowly distilled off until the free fatty acid content was 5% or less.

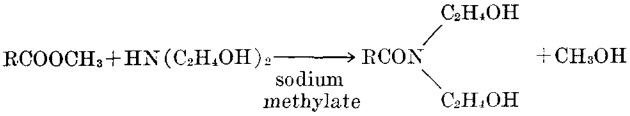


$$RCOOH + HN(C_2H_4OH)_2 \xrightarrow[\Delta]{} RCON\begin{matrix} / C_2H_4OH \\ \backslash C_2H_4OH \end{matrix} + H_2O$$

The final product was a clear, yellowish-brown, viscous liquid which was readily soluble in water, and had a pH of about 9.

The reaction product contained only 60–70% of pure coco-fatty acid diethanolamide, plus free amine, amine soap, fatty acid, fatty amide, esteramide, piperazine, and other compounds in lesser amounts.

In 1949 E. M. Meade was granted patents on the amidation of esters (2,3). His process reacted an ester with an amine containing a replaceable hydrogen attached to a nitrogen atom, in the presence of catalyst such as an alkali metal alcoholoxide. For example, a fatty methyl ester would be reacted with an alkyl amine at 100C for 3 hr in the presence of sodium methylate. In commercial practice, product purity as high as 92% is available.



$$RCOOCH_3 + HN(C_2H_4OH)_2 \xrightarrow[\text{sodium methylate}]{} RCON\begin{matrix} / C_2H_4OH \\ \backslash C_2H_4OH \end{matrix} + CH_3OH$$

Comparison of alkylolamides made by these two methods shows the difference in composition (4).

	Kritchevsky patent	Meade patent
Diethanolamine, %	29.0	7.0
Fatty acid, %	4.0	0.5
Ester amide, %	3.5	2.5
Fatty alkylolamide (by diff.), %	63.5	90.0

The purer alkylolamides have been called "extra" or "super" in comparison with the product made from fatty acids. The more active form is superior in its ability to stabilize foam and increase product viscosity (5).

The following work was conducted with methyl laurate at temperatures of 110–150C in a short-time, continuous reactor. The objective of this program was to save reaction time without sacrificing purity or quality.

Experimental

Experimental work was carried out in a thin-film evaporator. Figure 1 shows the detailed construction of this equipment, whereby spinning vanes spread

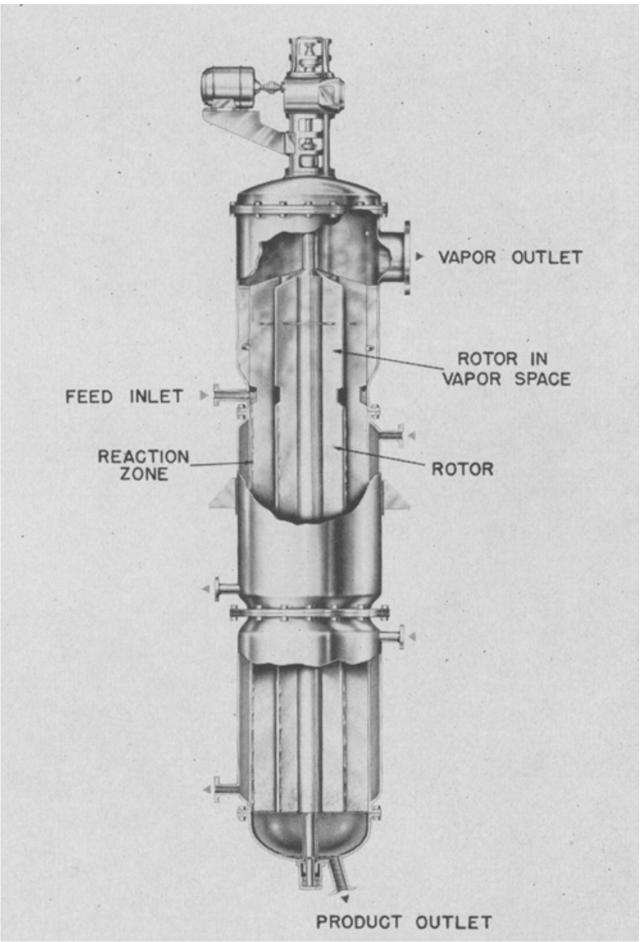


FIG. 1. Details of thin-film reactor.

liquid over the heat transfer surface. The high angular velocity (about 3600 rpm) of the rotor creates a turbulence in the liquid film which improves mass transfer of volatile reaction products into the vapor space where they are removed. The film thickness is between 1/32 and 1/16 in. Liquid reaction products flow down and out of the reactor into a receptacle which can be readily cooled. Figure 2 is a flow diagram of the process including feed and product streams.

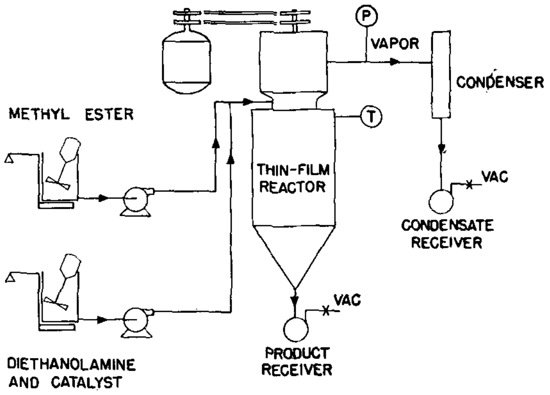


FIG. 2. Flow diagram of continuous alkylolamide process.

The first series of runs was made by reacting 1 mole of methyl laurate with 1.05 moles of diethanolamine and 0.044 mole, or 0.75% by weight, of KOH catalyst. KOH solution was added to diethanolamine, and this mixture was stripped of its water content by heat and vacuum prior to use. The flow rate into the reactor was held consistent at 1.38 lb per min for all runs except one, and the effective reaction area was 1 ft^2.

TABLE I

Effect of Temperature and Pressure on Reaction Yield

Run no.	Temperature		Absolute pressure, mm of Hg	Ester, %	Free diethanolamine, %	KOH, %	K soap, %	Alkylolamide, %
	°F	°C						
1	230	110	30	2.6	8.7	0.83	0.26	87.6
1a	230	110	30	2.2	10.0	0.87	0.27	86.7
2	230	110	760	42.0	0.9	0.29	1.48	55.3
3	260	127	12	2.9	....	....	....	....
4	295	146	15	3.2	....	....	....	....
5	295	146	60	5.2	0.7	0.59	0.74	92.8
6	300	149	115	3.1	4.7	0.51	0.60	91.1
6a	300	149	115	2.4	3.0	0.29	0.53	93.8
7	300	149	250	2.6	3.7	0.61	0.82	92.3
8	300	149	760	4.3	3.0	0.52	1.05	91.1
9[a]	300	149	10	3.5	....	....	....	....

[a] Run 9 was at an increased rate of 1.88 lb per min.

Table I shows the analysis of reaction products obtained from two series of runs, one essentially at 110C and the other at 149C. The absolute pressure was varied from 10 to 760 mm Hg. The amount of lauric diethanolamide in the reaction product will be called the "yield."

Table II presents yield data for a fixed operating temperature of 149C and absolute pressure of 406 mm Hg, while KOH catalyst content was varied from 0 to 0.20%. The mole ratio of methyl laurate to diethanolamine was 1 to 1.05.

TABLE II

Effect of KOH Catalyst Content on Yield

Run No.	KOH, %	Alkylolamide, %
1	0.00	0.0
2	0.05	91.6
3	0.10	89.6
4	0.20	94.6

TABLE III

Effect of Sodium Methylate Catalyst Content on Yield

Run No.	Sodium methylate, %	Alkylolamide, %
1	0.06	69.9
2	0.08	88.3
3	0.10	89.6
4	0.11	80.8
5	0.12	88.9
6	0.20	96.8
7	0.21	97.3
8	0.21	93.0
9	0.33	91.0

Table III presents data for 1 to 1.1 mole ratio of methyl laurate to diethanolamine, with sodium methylate (in alcoholic solution) as the catalyst. Catalyst was mixed into the diethanolamine stream. Operating temperature was 149C and the absolute pressure about 125 mm Hg.

Results and Discussion

The reaction between methyl laurate and diethanolamine results primarily in the formation of lauric diethanolamide and methanol. Removal of methanol would naturally drive the reaction to completion, and the combination of high temperature and low operating pressure favors this desirable effect. Figure 3 shows that absolute pressure had no effect on yield when the operating temperature was 149C. However, when the temperature was reduced to 110C, the beneficial effect of high vacuum was apparent in that the yield decreased from 87% to 55% in going from 30 mm Hg abs. to atmospheric pressure. Residence time in the evaporator was calculated at about 10 sec, while a conventional batch process may be at reaction temperature for 2–6 hr.

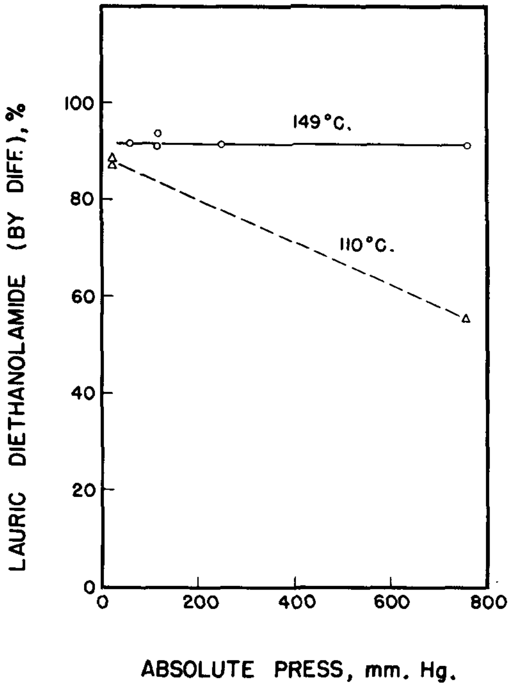


FIG. 3. Effect of temperature and pressure on yield of alkylolamides.

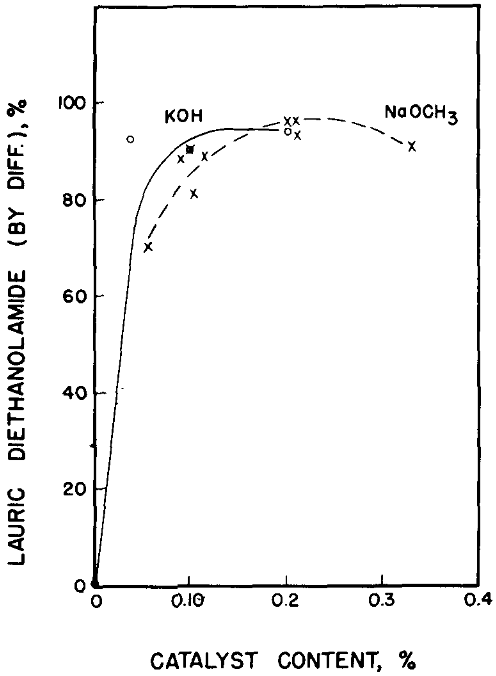


FIG. 4. Effect of catalyst content on yield of alkylolamides.

Figure 4 depicts the effect of catalyst quantity on yield. Similar results were obtained with KOH and sodium methylate, each giving a high yield at 0.2% catalyst content. The small catalyst usage plus the efficient removal of methanol and diethanolamine from the thin reaction zone both contributed to the high product purity. Therefore, it has been demonstrated that alylolamides can be made continuously at high temperatures (149C) while achieving a purity of 95–97%.

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Preparation of Foams from Vegetable Oil Derivatives

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Abstract

Dimer acid was hydroxyethylated at 110–240C in the presence of alkaline catalysts. Products having ethylene oxide: dimer acid mole ratios of 0.8 to 1.4 were transformed into flexible urethane foams of density 2.0 to 4.4 lb/ft^3. Hydrogenated "aldehyde oil" gave a rigid foam which had a density of 1.2 lb/ft^3.

IN THE SEARCH for inexpensive ingredients for commercial production of urethane foams, polyether types of polyols have largely taken over from the more expensive polyester types derived from polyols and polybasic acids. However, certain polyester polyols are still used in the clothing industry because of superior drape and feel. These polyols are from dimer acid and polyols such as diethylene glycol and trimethylolethane. Dimer acids are commercially available and are produced by the polymerization of polyunsaturated fatty acids derived from soybean, cottonseed, and linseed oils (1). Less expensive polyols should result from the condensation of ethylene oxide with dimer acid. The purpose of this paper is to describe the preparation of such polyols and to evaluate in a preliminary way urethane foams prepared from them.

In connection with a program now in progress at the Northern Laboratory, it became desirable to prepare foams from the polyol from an "aldehyde oil." These oils have been prepared by the ozonization of soybean or other vegetable oil followed by reductive decomposition of the ozonolysis solution to form aldehydic materials. After removal of solvent and volatile aldehydes, the residue, "aldehyde oil," should have the structure of a triglyceride of azelaic semialdehyde (2). The product obtained by the catalytic hydrogenation of this oil should have the structure of a triglyceride of 9-hydroxynonanoic acid. Departure from the ideal structures results from the presence of palmitic and stearic acids in the original soybean oil.

Experimental

Hydroxyethylated Dimer Acid. Polymerized fatty acid (Emery 3065-S) was the starting material. This brown liquid, consisting of three parts C_{36}-dibasic acid and one part C_{54}-tribasic acid, had an acid value of 188.5, a saponification value of 198.5, a neutralization equivalent of 297, a viscosity at 25C of 99 poises, and a Karl Fischer water content of 0.0%.

The condensation of ethylene oxide with dimer acid

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