Continuous Alkoxylation Process[1]

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ABSTRACT

A continuous process for the ethoxylation and propoxylation of fatty alcohols, alkyl phenols and fatty acids, based on the flow principle, is described. The short-time process developed on a pilot-plant scale leads to a high space-time yield in the presence of alkaline catalysts with complete conversion of the alkylene oxides at extremely short residence times of 10-80 sec. The products are of excellent quality.

INTRODUCTION

Most nonionics used today on an industrial scale are manufactured on the basis of fatty alcohols, alkyl phenols, fatty acids and fatty amines. Although large quantities of nonionics are produced, only discontinuous methods are applied. In the patent literature, some continuous alkoxylation processes are described. The most important have been published by the IG Farbenindustrie, Chemische Werke Huels, Oxirane, Montecatini, Distillers, and Union Carbide. They are based on the flow principle (1), spray (2) and column (3) techniques.

A review of the processes described in the literature has shown that it has not yet been possible to optimize all the factors important for a true continuous process. The processes generally have some of the following disadvantages: low space-time yield, incomplete reaction of the alkylene oxide, use of solvents, need for very expensive plant, and unsatisfactory quality of the end products.

EXPERIMENTAL PROCEDURES

The principle used by us is based on the flow technique, i.e., the process is carried out in reactors having cross sections that are small, compared to their lengths. We have tested various types of reactors. In this paper, only a special application of this principle will be described, namely the use of coiled tubes as reactors. For the reactions, two reactors of different size were used. The smaller reactor ("Reactor I," capacity of about 0.4 liters) had a pipe length of 15 m and an inner diameter of 6 mm; the bigger one ("Reactor II," capacity of about 0.8 liters) had a pipe length of 12.5 m and an inner diameter of 9 mm. Temperature measurement points were located every 2.5 m of pipe length in the smaller reactor and every 1.25 m in the larger one. In the bigger reactor, e.g., the first measuring point is located immediately before the entry into the reactor. Nine further points are located in the reactor, and the last measuring point is outside the reactor. Figure 1 shows a simplified flow sheet of the plant. The preheated starting material containing the catalyst is fed to a metering pump by way of filters and a measuring device; after passing a pressure control valve and a nonreturn valve, it is conveyed into a mixing chamber at a pressure of about 50 to 100 atm. The cooled alkylene oxide is also pumped into the mixing chamber from a weighing hopper after passing a brine cooler. A pressure gauge automatically switches off the plant if the pressure rises too high. A nonreturn valve is fitted but as a double precaution a flowmeter is installed. The temperature of the mixture is about 60-70 C. From the mixing chamber, the material passes through the actual reactor and is conveyed into a receiver by way of a pressure control valve and after passing a cooler. The reactor has the following design: the tubular high pressure reactor wound round a steam heated pipe is located in a pressurized heat exchanger filled with water; the reaction heat is removed by evaporation of water; the steam escaping through the valve is subsequently condensed, and the condensate is pumped back into the pressurized water jacket after being heated in an additional heat exchanger. A pump is installed in the heat exchanger system which circulates the water under

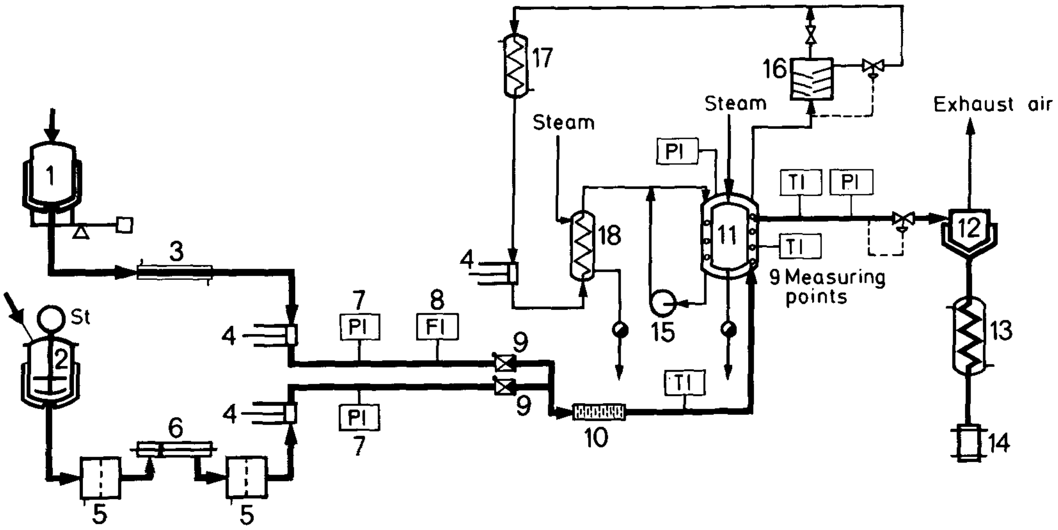

FIG. 1. Flow chart: continuous alkoxylation process: 1, alkylene oxide reservoir; 2, stock reservoir; 3, brine cooler; 4, metering pump; 5, filter; 6, measuring device; 7, pressure control valve; 8, flowmeter; 9, non-return valve; 10, mixing chamber; 11, reactor; 12, separator; 13, cooler 14, receiver; 15, circulating pump; 16, drop separator; 17, condenser; 18, heat exchanger.

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[1] Presented at the ISF-AOCS World Congress, Chicago, September 1970.

TABLE I

Ethoxylation of Fatty Alcohols and Alkylphenols[a]

Alcohol/ phenol	Catalyst concentration % Na	EO, mole	Maximum temperature C	Residence time, sec	Throughput, kg/hr	Glycols, %	Color (Lovibond 4 in cell)		
							yellow	red	blue
Lauryl alcohol	0.10	2.0	288	15	83[b]	1.6	0.7	0.1	0
$C_{12\text{-}14}$-alcohol	0.10	2.0	287	25	96[c]	1.7	1.0	0.1	0
Lauryl alcohol	0.20	4.0	249	130	10[b]	1.6	0.6	0.1	0
HD Ocenol (i.n. 50-55)	0.15	4.0	249	125	11[b]	3.2	9.0	1.0	0
Sec. C_{14}-alcohol (mixture of isomers)	0.04	2.0	281	42	57[c]	10.0	9.0	0.5	0
Lauryl alcohol + 2 PO	0.19	2.0	266	31	77[c]	------	8.0	0.6	0
Nonyl phenol	0.05	3.0	243	150	9[b]	-------	0.9	0.2	0

[a] Reaction conditions: $t_{\text{heat exchanger}}$ 183-235 C, P_{reactor}60-100 atm.

[b] Reactor I.

[c] Reactor II.

pressure. This enables a stable temperature control of the reaction. The whole plant has, of course, been equipped with a number of safety devices. The process was developed by us on a semitechnical scale.

The most important reaction variables were molar ratio of the starting material to alkylene oxide, catalyst, temperature, pressure and residence time of the product in the reactor. The effect of these factors on the course of the reaction was studied in detail and it was found that the following measures must be combined to obtain qualitatively good products with high space-time yields: (a) mole ratio of H-active compound to alkylene oxide = 1:1 to 1:6 per reaction stage; (b) catalyst concentration 0.01-1.5%, spec. 0.05-1.0% Na as $NaOCH_3$; (c) water content of initial reactants<0.1%; (d) maximum temp. 230-360 C, first part of the reactor 170-240 C, second part of the reactor 240-360 C; (e) pressure 50-100 atm; (f) residence time 8-150 sec, spec. 10-80 sec; (g) residence time in the reactor after passing through the maximum temperature not exceeding 5-30% of the total residence time; and (h) rapid cooling of the product to <100 C after leaving the reactor.

Under these conditions, it has been possible to achieve maximum throughputs of about 100 to 120 kg/hr in the bigger reactor with an actual capacity of 0.8 liters and a residence time of about 10 to 20 sec. This means that in this small reactor about 60 to 70 tons/month of alkylene oxide addition products can be produced.

DISCUSSION

Alkoxylation of Fatty Alcohols and Alkyl Phenols

As the alkoxylation of fatty alcohols is of great technical importance in the field of nonionics and ether sulfates, the process was studied especially thoroughly in this field. According to these studies, it is of essential importance that the maximum temperature is reached only shortly before discharge from the reactor. Table I shows experiments explaining the characteristics of the reaction control. The peak temperatures are, in general, 250 to 290 C. The maximum throughput is almost 100 kg of end product per hour. The polyglycol content mostly amounts only to 1% to 2% in the reaction of primary alcohols with 2 moles of EO. (Concerning the problems on the alkoxylation of secondary alcohols see references 4 and 5). In order to give an idea of the color quality of the products, the colors are given by the Lovibond method. It can be seen that using primary alcohols and alkyl phenols, practically colorless products are produced (6). The temperature curves of some reactions can be seen in Figure 2.

The experiments on the propoxylation of fatty alcohols and alkyl phenols (7) are given in Table II. For propoxylating, somewhat higher catalyst concentrations are required. The maximum temperature here can be 300 C. The temperature curves of the individual experiments are given

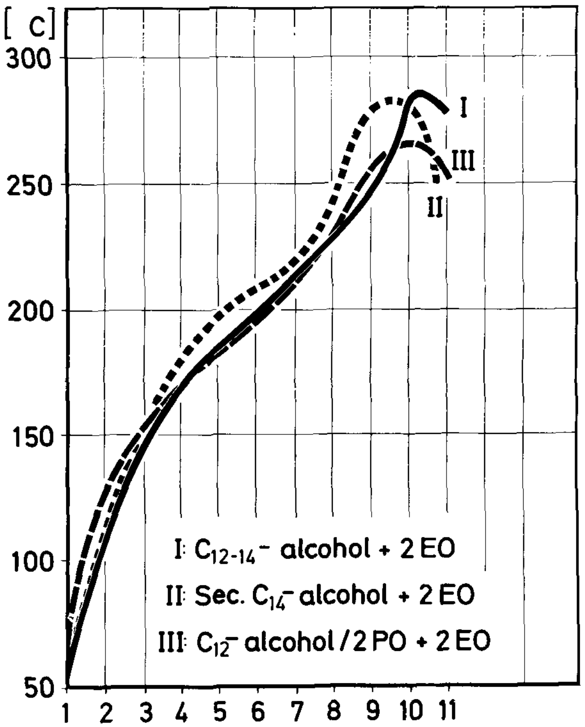

FIG. 2. Temperature curve of the ethoxylation of fatty alcohols (Reactor II).

TABLE II

Propoxylation of Fatty Alcohols and Alkylphenols[a]

Alcohol/ Phenol	Maximum temperature C	Residence time, sec	Throughput, kg/hr	Glycols, %	Color (Lovibond 4 in cell) yellow	red	blue
Lauryl alcohol	295	27	87	1.7	1.2	0.3	0
Lauryl alcohol	299	27	87	-----		Brown	
Oleylalcohol	282	25	93	2.9	9.5	0.4	0
$C_{12\text{-}14}$-alcohol + 2 EO	269	25	101	1.7	2.0	0.1	0
Nonyl phenol	301	37	71	0.8	5.6	0.3	0

[a]Reaction conditions: Reactor II, $t_{\text{heat exchanger}}$ 211-236C, p_{reactor}60-90 atm, catalyst concentration 0.3-0.4% Na, alkylene oxide added 2 PO.

TABLE III

Composition of Lauric Acid Alkylene Glycol Esters[a] (%)

Catalyst concentration, % Na	Alkylene oxide	Residence time, sec	Lauric acid	Glycols	Monoester	Diester
0.35	EO	55	0	1	77 (77)	22 (22)
	EO	37	2	0	83 (85)	15 (15)
	EO	28	11	1	76 (85)	12 (14)
0.40	EO	55	0	4	43 (43)	53 (53)
	EO	37	1	1	79 (80)	19 (19)
	EO	28	15	0	74 (87)	11 (13)
	PO	67	3	2	86 (89)	9 (9)
	PO	48	8	2	83 (90)	7 (8)
	PO	39	16	0	76 (91)	8 (9)
0.60	EO	55	0	10	19 (19)	71 (71)
	EO	37	0	11	22 (22)	67 (67)
	EO	28	0	10	21 (21)	69 (69)
0.65	PO	67	1	0	85 (86)	14 (14)
	PO	48	3	0	86 (89)	11 (11)
	PO	39	14	0	77 (90)	9 (10)

[a]Reaction conditions: Reactor II, $t_{\text{heat exchanger}}$ 225-235 C, $t_{\text{maximum reactor}}$ 240-260 C, p_{reactor} 50-100 atm.

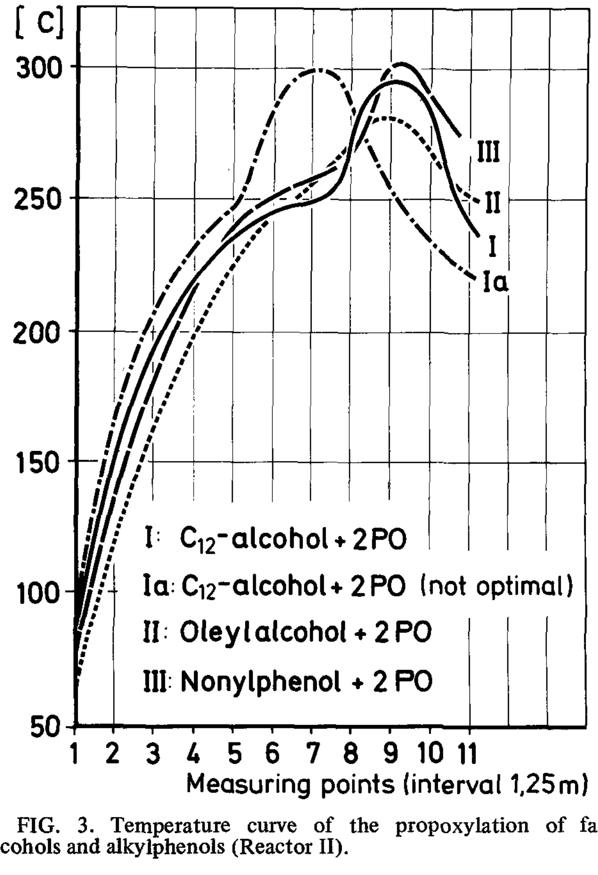

FIG. 3. Temperature curve of the propoxylation of fatty alcohols and alkylphenols (Reactor II).

in Figure 3. Here, too, it can be seen that the point at which the peak temperature is adjusted is of vital importance, and not only the absolute peak temperature (Curves I and Ia). In Curve Ia the peak temperature was prematurely reached, and thus a discolored product was produced.

The distribution of homologues of low alkoxylated products was examined and it was found that it is virtually the same as with addition products produced discontinuously. The nonionics and ether sulfates have the same properties as those produced by conventional methods.

Alkoxylation of Fatty Acids

In the reaction of carboxylic acids with 1 mole of ethylene oxide and in the presence of alkaline catalysts, monoesters should be produced in the first stage. The monoester reacts with more ethylene oxide to give polyglycolesters. However, such reaction products contain substantial amounts of the undesired by-products, diester and glycol, if the ethoxylation is done in the conventional way, e.g., 50% of diester and 14% of glycol (8). The application of special catalysts leads to high-grade alkyleneglycol fatty acid monoesters (9).

With our short-time reaction process, products with a high content of monoester should be produced, especially as it was to be expected that the side reactions can be suppressed in a process taking place in only a few seconds.

Table III gives the composition of ethoxylation products of lauric acid, depending on catalyst concentration and residence time. It can be seen that with a constant catalyst concentration and a decreasing residence time the content of free acid increases. If the acid contents are eliminated arithmetically (the values are given in parenthesis), the monoester contents are between 80% and 90% at a catalyst concentration of 0.35% of sodium. If the catalyst concentration is increased to 0.4%, the proportion of monoester will decrease substantially. Only with decreasing residence times does the content of monoester again increase to values between 80% and 90%. If the catalyst concentration is increased to 0.6% of sodium, products with only a very low content of monoester are obtained. In these cases in which little monoester is produced, the contents of glycol and diester increase correspondingly, and vice versa. Some reactions with propylene oxide are shown in Table III, too. Even with a catalyst concentration of 0.65% of sodium and a residence time of 67 sec, products are obtained containing 80% to 90% of monoester.

Products from the continuous short-time alkoxylation process have a monoester content twice as high as those produced in a discontinuous process (10). The temperature curve for ethoxylation and propoxylation of lauric acid is shown in Figure 4. With the alkoxylation of carboxylic acids, products of a perfect color are obtained, even if the temperature maximum does not occur just before discharge from the reactor. The products obtained, rich in monoester, are converted into water-soluble surfactants with good detergent properties.

Our studies show that long-chain alcohols, phenols and carboxylic acids can be continuously alkoxylated with reaction times of only a few seconds with complete conversion of the alkylene oxides. In comparison to the batch process, the continuous process offers the following advantages: extremely high space-time yields, constant product quality, and an especial suitability for the production of low-alkoxylated products in large quantities and of high-grade alkyleneglycol fatty acid monoesters.

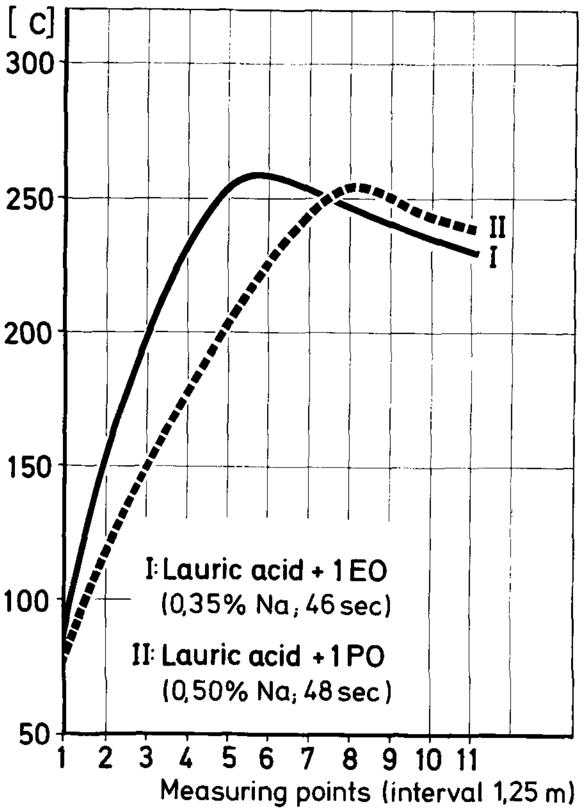

FIG. 4. Temperature curve of the alkoxylation of fatty acids (Reactor II).

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