INFLUENCE OF CATALYST ON METHOD OF PREPARATION AND PROPERTIES OF PENTAERYTHRITOL ESTERS

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Esters of neopentyl polyols with fatty acids are prepared by esterification in the presence of various catalysts such as sulfuric acid, p-toluenesulfonic acid, sodium bisulfate, various phosphorus compounds, zinc oxide, ion-exchange resins, etc. [1, 2]. The rate and degree of completion of the process, the method of treating the reaction products, and certain properties of the esters that are synthesized are totally dependent on which catalyst is used.

Notwithstanding the large amount of literature available in this area, it is practically impossible to determine the specific advantages and disadvantages of the individual compounds used as catalysts for the esterification reaction.

We have studied different compounds with a view toward determining the most effective catalyst for the synthesis of pentaerythritol esters.

The criteria that we used for rating these catalysts were the thermal stability of the ester product and the relative ease or difficulty of recovering the ester from the reaction mixture.

The esterification was carried out in a four-necked flask with continuous stirring of the product mixture under nitrogen, with a 10% excess of the fatty acid (relative to the stoichiometric quantity).

The reaction rate was monitored on the basis of the amount of water evolved and the acid number of the esterified product. The degree of esterification was determined on the basis of the hydroxyl number of the ester after distilling off the unreacted starting materials.

The materials studied as catalysts were sulfuric acid with activated carbon, sodium bisulfate, tributyl phosphate, and tributyl phosphite. The schemes for synthesizing the pentaerythritol esters in the presence of the different catalysts were as follows:

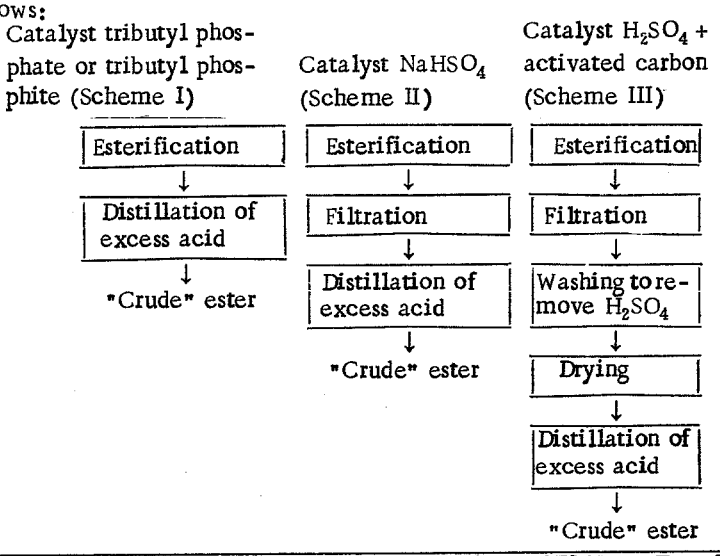

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TABLE 1. Synthesis of Pentaerythritol Esters in the Presence of Various Catalysts

	Catalyst for esterification reaction			
	tributyl phosphate	tributyl phosphite	sodium bisulfate	sulfuric acid with activated carbon
Quantity of catalyst, % of charge	2	2	5	1+1
Reaction temperature, °C	160—200	160—200	160—200	160—200
Reaction time, h	10	10	10	10
Ester yield, %				
"crude"	99,5	99,4	92,5	84,4
finished	85	82	72	67
Content of triesters, %	0,9	0,8	0,4	0,4
Color of esterified product, NPA	1	1	2	3

TABLE 2. Characteristics of Pentaerythritol Esters

	Pentaerythritol ester obtained with indicated catalyst			
	tributyl phosphate	tributyl phosphite	sodium bisulfate	sulfuric acid with activated carbon
Acid No., mg KOH/g	0,02	0,02	0,03	0,03
Ester No., mg KOH/g	398	400	402	401
Hydroxyl No., mg KOH/g	1,2	None	0,5	0,5
Solid point, °C	—60	—60	—60	—60
Viscosity (cSt) at indicated temperature				
100°C	4,40	4,42	4,45	4,45
50°C	16,4	16,6	16,8	16,8
—40°C	5500	5650	5700	5700
Boiling point, °C	240—290	242—285	243—295	255—290
Content of catalyst elements, %	0,02 (P)	0,04 (P)	0,03 (S)	0,02 (S)
Ester component composition (by GLC), %				
C_{25}	0,9	0,8	0,4	0,4
C_{25}	0,6	1,3	1,5	0,8
C_{26}	2,4	2,9	2,7	2,1
C_{27}	6,1	5,6	5,1	4,5
C_{28}	8,1	9,1	8,9	9,1
C_{29}	10,9	12,2	13,5	12,5
C_{30}	14,4	15,3	16,4	16,1
C_{31}	15,6	15,5	15,9	16,6
C_{32}	14,7	13,7	14,4	15,2
C_{33}	10,9	10,4	10,6	11,1
C_{34}	8,2	7,5	6,3	7,1
C_{35}	6,0	4,1	3,2	3,8
C_{36}	1,2	1,6	0,7	0,7

With any of these catalysts present, the esterification of pentaerythritol with a C_5-C_9 fatty acid cut goes essentially to 100% completion within 10 h at temperatures of 100-200°C. The esterified products obtained with tributyl phosphate or tributyl phosphite are less highly colored than those obtained with catalysts based on sulfuric acid (Table 1).

The esterified product was treated to remove excess acids and catalyst, thus producing the so-called crude ester. When using a homogeneous catalyst (ester of phosphoric or phosphorous acid), the catalyst was distilled off from the esterified product along with the excess fatty acids, and the yield of crude ester amounted to more than 99%.

When using sodium bisulfate as the catalyst, the esterified product was subjected to filtration; when using sulfuric acid with activated carbon as the catalyst, the esterified product after filtration was washed and dried under vacuum. All these operations complicate the process technology by increasing the number of stages and also lead to considerably lower yields of the crude ester.

TABLE 3. Thermal-Oxidative Stability of Pentaerythritol Esters in 50-h Tests at 225°C with Metal Strips and with Various Additive Packages

	Pentaerythritol ester obtained with indicated catalyst			
	tributyl phosphate	tributyl phosphite	sodium bisulfate	sulfuric acid with activated carbon
Acid No., mg KOH/g	9.9	16.7	17.7	10.5
% Viscosity change $\Delta\nu$				
at 50°C	58	96	64	58
at 100°C	48	67	46	43
Copper corrosion, mg/cm^2	0.18	0.579	0.67	0.23
Sediment insoluble in isooctane, %	0.6	1.2	5.2	4.5

The crude esters were distilled at 280-320°C at an absolute pressure of 1-2 mm Hg and were then neutralized with 3% NaOH solution and finished by treatment with adsorbents.

The finished esters were examined to determine their physical and chemical properties and thermal-oxidative stability. Also, the ester compositions were determined by gas–liquid chromatography [3]. The data listed in Table 2 indicate that neither the component composition nor the properties of the esters are influenced by the catalyst used in the esterification reaction. However, the choice of catalyst does have a substantial influence on the stability of the esters (Table 3).

The most stable esters proved to be those synthesized in the presence of tributyl phosphate. The esters synthesized in the presence of sulfuric acid with activated carbon were very nearly as good in all respects except that they formed large amounts of isooctane-insoluble sediment.

The esters synthesized with tributyl phosphite or sodium bisulfate as a catalyst gave higher acid numbers after oxidation, large amounts of sediment, and high levels of copper corrosion.

If the esterification reaction is conducted in the presence of sulfuric acid without the activated carbon, large amounts of tarry compounds are formed, and the esters are considerably poorer in thermal-oxidative stability.

The differences in oxidative stability of the esters can apparently be explained on the basis that interaction of the starting materials with the catalyst during the course of the esterification gives rise to by-products consisting of high-molecular-weight mixed esters of phosphoric, phosphorous, or sulfuric acid along with the fatty acids and pentaerythritol. This statement is supported by the fact that elements of the catalyst are present in the esters after treating to remove the catalyst, and even in the finished esters after vacuum distillation. Apparently the mixed esters of phosphoric acid have a stabilizing effect on the pentaerythritol ester, in contrast to the effect of the esters of phosphorous or sulfuric acid.

Of all the catalysts studied for the esterification of pentaerythritol with fatty acids, the most desirable is the tributyl phosphate. The main advantages of this catalyst are the high level of thermal-oxidative stability of the esters that are produced and the ease of removal of the tributyl phosphate from the esterified product.

LITERATURE CITED

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