Published Apr. 20, 1943

Serial No. 374,298

ALIEN PROPERTY CUSTODIAN

METHOD OF INFLUENCING THE POLYMERIZATION AND THE PROPERTIES OF THE OBTAINED PRODUCTS

Willy O. Herrmann, Deisenhofen, and Wolfram Haehnel, Munich, Germany; vested in the Alien Property Custodian

No Drawing. Application filed January 13, 1941

Surprisingly it has been found that polymerization reactions and the polymers obtained thereby may be influenced by an addition of vinyl crotonate. Thereby the grade of polymerization increases so much as not known until now, and the properties of the polymers vary in a wide range, whereby even unknown properties may be obtained. Herein lies the technical value of this invention and its significant progress.

Until now, it was impossible to produce a vinyl acetate insoluble in all solvents. The use of vinyl crotonate according to this invention solves this problem. Furtheron it is also possible to produce the most various polymers out of the same monomeric starting material, e. g. vinyl acetate, though exactly the same condition and the same apparatus are applied. In order to obtain these various polymers, it is only necessary to vary the amount of the added vinyl crotonate, whereby even very small amounts of this substance change the properties of the polymers. In such a way polymers of a desired solubility, capability of swelling, and a determined melting point and various thermoplasticity are attainable.

The described effect of vinyl crotonate upon the polymerization of vinyl acetate is also attainable if other polymerizable compounds like other vinyl or acrylic compounds or mixtures of polymerizable compounds are subjected to polymerization in the presence of vinyl crotonate.

This discovery of the surprising and specific effect of vinyl crotonate seems also to clear up some striking facts: e. g. the higher activity of vinyl acetate which was produced in former times and the insolubility of the polymers in spirit are probably due to the presence of an insignificant amount of vinyl crotonate. Hence follows that later on when vinyl acetate could be produced in a pure state, the activity of vinyl acetate and the insolubility of the polymers in spirit disappeared, and that it was necessary to discover the effect of vinyl crotonate in order to obtain the mentioned properties.

The polymers obtained according to this invention may not only be applied in the known way but also in a wider range, which is determined by the new attainable properties of the polymers like insolubility, larger mechanical capability of resistance, infusibility, diminished thermoplasticity, absence of cold flow and so on. E. g. the vinyl acetates according to the invention can now be also applied for the production of pressed articles and the like, if a small thermoplasticity is desired.

Example 1

Monomeric vinyl acetate mixed with the same volume of alcohol was polymerized under addition of 1% of benzoylperoxide (calculated upon the applied vinyl acetate). In a quiet course of polymerization a polyvinyl acetate, solved in alcohol, was obtained which is soluble in acetone, benzene, acetic ester, and many other solvents, melting at 110°.

If the experiment was repeated in the presence of 1% of vinyl crotonate the polymerization took place very violently. The polymer precipitated in form of a gelatinous mass and was infusible and insoluble in solvents.

Example 2

5 mixtures of 30 per cent by volume of spirit and 70 per cent by volume of vinyl acetate were polymerized with 1% of benzoylperoxide by heating. Thereby 1, 2, 3, 7 and 10% vinyl crotonate, calculated upon the applied vinyl acetate, were added. The result was that the obtained polymers had various melting points and various capabilities of swelling. In the following table, the numbers mentioned under "capability of swelling" means volume relation in per cents between the swelled and non-swelled material.

Vinyl crotonate added per cent	Capability of swelling			Melting point
	In spirit	In acetone	In benzene	
				Degrees
1	(1)	(1)	(1)	116
2	(1)	(1)	(1)	195
3	463	1,093	1,098	(2)
7	384	885	807	(2)
10	273	825	724	(2)

[1] Soluble.
[2] Infusible.

Example 3

Pure vinyl acetate was enclosed in glass tubes and polymerized under an addition of 1 or 10% vinyl crotonate by sun light. Infusible polymers, insoluble in alcohol, acetone and benzene were obtained. Following a table about the capability of swelling as in example 2.

Vinyl crotonate added per cent	Capability of swelling		
	In spirit	In acetone	In benzene
1	217	639	458
10	157	356	332

In the absence of vinyl crotonate, products are obtained which are hardly soluble in spirit but soluble without any difficulty in acetone and benzene.

Example 4

2 mixtures consisting of 9 parts by weight of ethyl alcohol and 21 parts by weight of vinyl formiate were polymerized by heating with 0.2 parts by weight of benzoylperoxide, whereby in one case 0.2 parts by weight of vinyl crotonate were added. The solubility of the polymers differs as follows:

	Made with vinylcrotonate	Made without vinylcrotonate
In acetone	Insoluble	Soluble.
In formic acid	do	Do.
In chloroform	do	Do.
In dioxane	do	Do.
In acetic acid	do	Do.
In pyridine	do	Do.

Example 5

56 g of monomeric vinyl chloride solved in 500 g of methyl alcohol were polymerized by active light whereby the formed polyvinylchloride was obtained in a form of a white powder. The polymer was clearly soluble in hot and cold dioxane. The same polymerization in the presence of 0,56 g vinyl crotonate yielded a polymer unsoluble even in boiling dioxane.

Example 6

240 g of monomeric vinyl acetate were emulsified under stirring with 200 g of a aqueous solution of polyvinyl alcohol of 6%. The emulsion was polymerized by slow heating in the presence of 1 ccm of hydrogen peroxide of 30%. The polymer, an emulsion of polyvinyl acetate which may be diluted homogeniously with water, yielded with methyl alcohol a clear solution.

A repetition of this polymerization in the precence of 2,4 g of vinyl crotonate yielded a coarse-grained paste which could not more homogeniously diluted with water and the substance of which was not soluble in methanol.

The same polymerization in the presence of 0,5 g of vinyl crotonate yielded an emulsion which could be diluted homogeniously with water. But after some hours a precipitate was formed which was nearly not soluble in methyl alcohol.

In this way the physical character of an emulsion and its behaviour against solvents may be varied in a wide range.

Example 7

A mixture of 86 g of vinyl acetate and 263 g of trichloroethylene was boiled in the presence of 5,2 g of benzoylperoxide for 5½ hours whereby the co-polymerization of the two unsaturated monomers passed various intermediate stages and finally gave a mixed polymer with the brutto formula of $C_8H_7O_2Cl_3$. By purification with water steam and by precipitating the solution in aceton with water, a polymer was obtained in the form of a white, light powder. This product easily solves in many organic solvents, specially in ether and methylalcohol.

The same polymerization in the presence of 0,9 g of vinyl crotonate yielded a co-polymer hardly solving in ether and unsoluble in methyl alcohol.

It will be understood, of course, that the invention is not limited to the special amounts of applied vinyl crotonate set forth in the examples for the purpose of disclosure, but is capable of considerable modification of this amounts. The effect of vinyl crotonate according to this invention is attainable with amounts of 0,1 to a few per cent of this substance. The more vinyl crotonate is applied, the more increases the molecular weight of the obtained polymers. But there has been found, that an addition of more than a few per cent of this substance does not increase the effect but yields co-polymers of vinyl crotonate with the starting material to be polymerized.

WILLY O. HERRMANN.
WOLFRAM HAEHNEL.