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(71) **Demandeur/Applicant**:
OXENO OLEFINCHEMIE GMBH, DE

(72) **Inventeurs/Inventors**:
GRASS, MICHAEL, DE;
KOCH, JURGEN, DE

(74) **Agent**: FETHERSTONHAUGH & CO.

(54) **Titre** : BENZOATES D'ISONONYLE ET LEUR UTILISATION
(54) **Title**: ISONONYL BENZOATES AND THEIR USE

(57) **Abrégé/Abstract**:
The invention relates to isomeric nonyl benzoates, processes for their preparation, mixtures of the benzoates with alkyl phthalate, alkyl adipate, or alkyl cyclohexanedicarboxylate, and also to the use of these mixtures. The isomeric nonyl benzoates are produced from isomeric nonyl alcohols having a content of 3,5,5-trimethylhexanol of less than 10 mol%. The isomeric nonyl benzoates are useful as a plasticizer of plastics such as polyvinyl chloride, either alone or in combination with the alkyl phthalate, alkyl adipate or alkyl cyclohexanedicarboxylate.

Abstract

The invention relates to isomeric nonyl benzoates, processes for their preparation, mixtures of the benzoates with alkyl phthalate, alkyl adipate, or alkyl cyclohexanedicarboxylate, and also to the use of these mixtures. The isomeric nonyl benzoates are produced from isomeric nonyl alcohols having a content of 3,5,5-trimethylhexanol of less than 10 mol%. The isomeric nonyl benzoates are useful as a plasticizer of plastics such as polyvinyl chloride, either alone or in combination with the alkyl phthalate, alkyl adipate or alkyl cyclohexanedicarboxylate.

Isononyl benzoates and their use

The invention relates to isomeric nonyl benzoates, processes for their preparation, mixtures of the same with alkyl phthalates, alkyl adipates, or alkyl cyclohexanedicarboxylates, and also to the use of these mixtures.

Polyvinyl chloride (PVC) is one of the most commercially important polymers. It has a wide variety of uses both in the form of unplasticized PVC and in the form of plasticized PVC.

To produce a plasticized PVC, plasticizers are added to the PVC, those used in the majority of cases being phthalates, in particular di-2-ethylhexyl phthalate (DEHP), diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP). As the chain length of the esters increases, the solvation or gelation temperatures rise, and the processing temperatures of the plasticized PVC therefore rise. The processing temperatures can be reduced by adding what are known as rapid gellers, such as the short-chain phthalates e.g., dibutyl phthalate (DBP), diisobutyl phthalate (DIBP), benzyl butyl phthalate (BBP), or diisoheptyl phthalate (DIHP). Alongside the short-chain phthalates, dibenzoates, such as dipropylene glycol dibenzoates, or the like, may be used for the same purpose.
These rapid-gellers often lead to a marked rise in viscosity with time in PVC plastisols, due to their high solvating power. In many cases this has to be compensated by adding (often expensive) viscosity reducers.

A general demand during the preparation of PVC plastisols is low viscosity and minimum gelling temperature. Long shelf life (little increase in viscosity with time) for the plastisol is another desirable feature.
High viscosity would be disadvantageous during processing of the plastisol in machinery. An excessively high gelling temperature would lead to discoloration due to thermal stress.

There are almost no known plasticizers which give a significant lowering of the gelling temperature in formulations and also maintain the viscosity of the plastisol at a low level even after storage for a period of several days. 2-Ethylhexyl benzoate has recently been proposed as a product which could comply with these requirements [Bohnert, Stanhope, J. Vinyl Addit. Technol. (2000), 6(3), 146-149]. However, this compound has comparatively high vapor pressure, and this often leads to unacceptable losses of the compound during processing.

German Patent Publication No. (DE) 19 62 500 discloses the use of a mixture of relatively long-chain esters of benzoic acid and phthalic acid for preparing plastisols. 3,5,5-Trimethylhexanol is preferably used for preparing the benzoates. No precise information is given concerning the phthalic diesters to be used.

The use of phthalates whose ester groups have from 1 to 8 carbon atoms is subject to increasing restriction for reasons of toxicology. Esters having relatively long alkyl side chains are classified as less toxicologically hazardous, but have poorer processing properties.

There is a scope for improving the gelling properties, the low-temperature flexibility and the shelf life of the above-mentioned plasticizer systems in PVC.

It was therefore desired to find novel plasticizers for plastics, e.g. for PVC, which are based on low-cost raw materials and have equivalent or improved plasticizer properties, such as improved low-temperature-flexibilizing power and lower volatility, while their plastisols have the lower viscosity level.

It has now been found that isononyl benzoates, alone or in a mixture with phthalic esters, dialkyl adipates, or cyclohexyldicarboxylic esters have the desired performance profiles.

The present invention therefore provides mixtures of isomeric isononyl benzoates, wherein nonyl alcohols obtained by saponifying the isomeric isononyl benzoates comprise less than 10 mol% of 3,5,5-trimethylhexanol.

The present invention also provides processes for preparing mixtures of isomeric isononyl benzoates by esterifying benzoic acid with nonyl alcohols which comprise less than 10 mol% of 3,5,5-trimethylhexanol, or by transesterifying one or more alkyl benzoates whose alkyl radicals contain from 1 to 8 carbon atoms with nonyl alcohols which comprise less than 10 mol% of 3,5,5-trimethylhexanol.

Fig 1. shows the viscosity/temperature curve ("gelling curve") relevant for the onset of gelling.

The saponification of the benzoic esters or the other esters mentioned below may be carried out by conventional methods via reaction with alkaline media (see, for example, Ullmann's Enzyklopädie der Technischen Chemie [Ullmann's Encyclopedia of Industrial Chemistry], 5th Edn. A 10, pp. 254-260).

The nonyl alcohols used to prepare the mixtures of the isomeric isononyl benzoates of the invention are generally isomer mixtures and are often termed isononanols or isononyl alcohols. The mixtures of the isomeric isononyl benzoates or the nonyl alcohols used in the process of the invention have high linearity, characterized by the proportion of less than 10 mol% (0-10), preferably less than 5 (0-5) mol%, particularly preferably less than 2 (0-2) mol%, of 3,5,5-trimethylhexanol. These data are applicable to all of the mixtures mentioned below. Mixtures of this type are commercially available with the CAS numbers 27458-94-2, 68515-81-1, 68527-05-9, or 68526-84-1 and usually contain up to about 10 various linear and branched alcohols having 9 carbon atoms as their main components.

"CAS Number" means Chemical Abstracts Registry Number. The isomer distributions of the nonyl radicals may be determined using the usual test methods familiar to the skilled worker, for example NMR spectroscopy, GC, or GC/MS spectroscopy.

The nonyl benzylates of the invention may be used as viscosity reducers and rapid-gelling plasticizers, and when compared with known systems in the modification of plastics, such as PVC, very advantageously combine low volatility, good gelling capability, good low-temperature flexibilization, and little rise in viscosity in plastisols. In one version of the process, one or more alkyl benzoates are transesterified, preferably methyl benzoate, ethyl benzoate, propyl benzoate, isobutyl benzoate, amyl benzoate, and/or butyl benzoate.

For preparing the isononyl benzoates of the invention, and also the cyclohexanedicarboxylic esters, the nonyl adipates and/or nonyl phthalates are used, it is preferable to use industrial nonanol mixtures, i.e. mixtures of the isomeric alcohols, hereinafter termed isononanol or isononanol mixture.

The isomer distribution in these mixtures is determined by the nature of the preparation process of the nonyl alcohol (isononanol) used.

Isononanol is prepared by hydroformylating octenes, which in turn are produced in various ways. Industrial C_4 olefins are the raw material generally used for this purpose, and initially comprise all of the isomeric C_4 olefins alongside the saturated butanes and, optionally, contaminants, such as C_3 and C_5 olefins and acetylenic compounds. Oligomerization of this olefin mixture gives mainly isomeric octene mixtures alongside higher oligomers, such as C_{12} and C_{16} olefin mixtures.

These octene mixtures are hydroformylated to give the corresponding aldehydes and then hydrogenated to give the alcohol.

The composition of, i.e. the isomer distribution in, industrial nonanol mixtures depends on the starting material and on the oligomerization and hydroformylation processes. Any of these mixtures may be used to prepare the esters of the invention. Preferred nonanol mixtures are those obtained by hydroformylating C_8 olefin mixtures obtained by oligomerizing substantively linear butenes (i.e., n-butenes also known as di-n-butenes, namely, 1-butene and 2-butene) on nickel supported catalysts (e.g. the OCTOL* process), in the presence of unmodified cobalt compounds, followed by hydrogenation of the catalyst-depleted hydroformylation mixture. The C_8 olefin mixture is composed mainly of linear octenes (about 2-20%), 3-methylheptenes (about 50-70%) and 3,4-dimethylheptenes (about 20-30%). The proportion of isobutene in the starting material (i.e., the isomeric C_4 olefins) here, based on total butene content, is less than 5% by weight, preferably less than 3% by weight, particularly preferably less than 1% by weight. The result of this is that the proportion of more highly branched nonanol isomers, including, inter alia, 3,5,5-trimethylhexanol, which has proven less advantageous, is markedly suppressed. Mixtures of the isomeric isononyl benzoates of the invention therefore comprise less than 10% by weight, preferably less than 5% by weight, particularly preferably less than 3% by weight, in particular less than 1% by weight, of benzoic acid esters of 3,5,5-trimethylhexanol. These data are based on the alcohol mixtures which would result from saponification of the ester mixtures of the invention.

*Trade-mark

For preferred methods of preparing the isononyl alcohol mixtures, see for example, Canadian Patent Application Nos. 2,282,215 (laid-open Mar. 16, 2000); 2,282,148 (laid-open Mar. 16, 2000); 2,281,162 (laid-open Mar. 16, 2000); 2,364,826 (laid-open June 14, 2002); 2,282,949 (laid-open March 16, 2000); and 2,225,773 (laid-open June 24, 1998). For preferred methods of the hydroformylation, see for example, Canadian Patent Application Nos. 2,353,061 (laid-open Jan. 14, 2002); 2,327,022 (laid-open May 30, 2001); 2,325,676 (laid-open May 12, 2001).

The present invention also provides alkyl benzoate mixtures from which the alcohol mixture obtained by saponification corresponds to the alcohols with CAS numbers 68551-09-7, 91994-92-2, 68526-83-0, 66455-17-2, 68551-08-6, 85631-14-7, or 97552-90-4.

These are alcohol mixtures which also comprise, alongside the isononyl alcohols mentioned, alcohols having from 7 to 15 carbon atoms (in accordance with CAS definition).

The present invention also provides mixtures of the isononyl benzoates, preferably the abovementioned isononyl benzoates with, dialkyl phthalates, preferably diisononyl phthalate, or with dialkyl adipates, preferably diisononyl adipates, or with alkyl cyclohexanedicarboxylates, preferably diisononyl cyclohexanedicarboxylates.

These mixtures of the invention may be defined as follows:

a) Mixtures comprising (A) from 1 to 99% by weight, preferably 10 to 50% by weight, of isomeric isononyl benzoates, where the nonyl alcohols obtained by saponifying these benzoates comprise less than 10 mol% of

3,5,5-trimethylhexanol, and (B) from 99 to 1% by weight, preferably 90 to 50% by weight of dialkyl phthalates whose alkyl radicals contain from 4 to 13 carbon atoms. The weight percentages are based on the total amount of the ingredients (A) and (B).

Preferred phthalic esters are diisononyl phthalates. In particular, the isononanols obtained by saponifying the diisononyl phthalates comprise less than 10 mol% of 3,5,5-trimethylhexanol.

b) Mixtures comprising (A) from 1 to 99% by weight, preferably 10 to 50% by weight, of isomeric isononyl benzoates, where the nonyl alcohols obtained by saponifying these benzoates comprise less than 10 mol% of 3,5,5-trimethylhexanol, and (C) from 99 to 1% by weight, preferably 90 to 50% by weight, of alkyl adipates whose alkyl radicals contain from 4 to 13 carbon atoms. The weight percentages are based on the total amount of the ingredients (A) and (C).

Preferred alkyl adipate is diisononyl adipate. It is particularly preferable that the isononyls obtained by saponifying the diisononyl adipates comprise less than 10 mol% of 3,5,5-trimethylhexanol.

c) Mixtures comprising (A) from 1 to 99% by weight, preferably 10 to 50% by weight, of isomeric isononyl benzoates, where the nonyl alcohols obtained by saponifying these benzoates comprise less than 10 mol% of 3,5,5-trimethylhexanol, and (D) from 99 to 1% by weight, preferably 90 to 50% by weight, of alkyl cyclohexanedicarboxylate whose alkyl radicals contain from 4 to 13 carbon atoms. The weight percentages are based on the total amount of the ingredients (A) and (D).

Preferred dialkyl cyclohexanedicarboxylate is diisononyl cyclohexanedicarboxylate. It is particularly preferable that the isononanols obtained by saponifying the isononyl cyclohexanedicarboxylates comprise less than 10 mol% of 3,5,5-trimethylhexanol. Among the cyclohexanedicarboxylic esters, preference is in turn given to those having 1,2-positioned carboxy groups.

In each of the mixtures, the proportions of the esters mentioned give 100% in total.

Mixtures of the invention are defined via the composition of the esters mentioned, not via the nature or sequence of preparation of the mixtures. Mixtures of the present invention are also present when the esters mentioned are mixed in the ratio mentioned, simultaneously or in succession, with another substance, such as plastics, (e.g. PVC).

An autocatalytic or catalytic method, for example one using Brönsted acids or Lewis acids, may be used to esterify the benzoic acid, phthalic acid, phthalic anhydride, adipic acid, cyclohexanedicarboxylic acid or its anhydride with an isomerically pure nonanol or with an isononal mixture to give the corresponding esters. Quite irrespective of the nature of the catalysis selected, the result is always a temperature-dependent equilibrium between the starting materials (acid and alcohol) and the products (ester and water). In order to shift the equilibrium in favor of the ester, use may be made of an entrainer with the aid of which the water of reaction is removed from the mixture. Since the alcohol mixtures used for the esterification process have lower boiling points than the benzoic acid and its esters and are not fully measurable with water, they are often used as an entrainer which can be returned to the process after water-separation.

The alcohol or, respectively, isomeric alcohol mixture used to form the ester and simultaneously as entrainer is used in excess, this preferably being from 5 to 50%, in particular from 10 to 30%, of the amount needed to form the ester.

Esterification catalysts which may be used are acids, such as sulfuric acid, methane sulfonic acid, p-toluenesulfonic acid, metals, or their compounds. Examples are tin, titanium, and zirconium, and these may be used in the form of finely divided metals, or advantageously in the form of their salts, oxides, or soluble organic compounds. Unlike protonic acids, the metal catalysts are high-temperature catalysts whose full activity is often not achieved until temperatures reach above 180°C. However, their use is preferred since the level of formation of by-products, such as olefins from the alcohol used, is lower when comparison is made with protonic catalysis. Examples representing metal catalysts are tin powder, stannous oxide, stannous oxalate, titanium esters, such as tetraisopropyl orthotitanate or tetrabutyl orthotitanate, and zirconium esters, such as tetrabutyl zirconate.

The concentration of catalyst depends on the nature of the catalyst. In the case of the titanium compounds whose use is preferred, it is from 0.005 to 1.0% by weight, based on the reaction mixture, in particular from 0.01 to 0.5% by weight, very particularly from 0.01 to 0.1% by weight.

When titanium catalysts are used, the reaction temperatures are from 160 to 270°C, preferably from 180 to 250°C. The ideal temperatures depend on the starting materials, the progress of the reaction, and the concentration of catalyst. They may readily be determined by trials for each individual case. Higher temperatures increase the reaction rates and favor side reactions, such as elimination of water from alcohols or formation of colored by-products. For removal of the water of reaction, it is advantageous that the alcohol can be distilled off from the reaction mixture. The desired temperature or the desired temperature range may be set via the pressure in the reaction vessel. For this reason, the reaction is carried out at superatmospheric pressure in the case of low-boiling alcohols, and at subatmospheric pressure in the case of relatively high-boiling alcohols. For example, operations for the reaction of benzoic acid with a mixture of isomeric nonanols are carried out in a range of temperature from 170 to 250°C in the range of pressures from 1 bar to 10 mbar.

Some or all of the liquid to be returned to the reaction may be composed of alcohol obtained by work-up of the azeotropic distillate. It is also possible to carry out the work-up at a later juncture, and to replace some or all of the amount of liquid removed by fresh alcohol, i.e. alcohol provided in a feed vessel.

The crude ester mixtures, which comprise by-products as well as the ester(s), alcohol, and catalyst or products derived from the catalyst, are worked up by processes known per se. This work-up encompasses the following steps: removal of the excess alcohol and, where appropriate, low-boilers, neutralization of the acids present, and optional steam distillation, conversion of the catalyst into a residue which is easy to filter, removal of the solids, and, where appropriate, drying. The sequence of these steps may differ, depending on the work-up process used.

The nonyl ester or the mixture of the nonyl esters may be removed from the reaction mixture by distillation, where appropriate after neutralization of the mixture.

As an alternative, the nonyl benzoates of the invention may be obtained by transesterifying a benzoic ester with nonanol or with an isononanol mixture. The starting materials used comprise benzoic esters whose alkyl radicals bonded to the O atom of the ester group contain from 1 to 8 carbon atoms. These radicals may be aliphatic, straight-chain or branched, alicyclic, or aromatic. One or more methylene groups in these alkyl radicals may have been substituted by oxygen. It is advantageous that the alcohols on which the starting ester is based have lower boiling points than the isononanol mixture or nonanol used. Methyl benzoate is a preferred starting material.

The transesterification is carried out catalytically, for example using Brönsted or Lewis acids, or using bases. Quite irrespective of the catalyst used, the result is always a temperature-dependent equilibrium between the solid material (alkyl benzoate and isononanol mixture or nonanol) and the products (nonyl ester or nonyl ester mixture and liberated alcohol). In order to shift the equilibrium in favor of the nonyl ester or of the isononyl ester mixture, the alcohol produced from the starting ester is distilled off from the reaction mixture.

Here, too, it is advantageous to use excess of the isononanol mixture or, respectively, nonanol.

Transesterification catalysts which may be used are acids, such as sulfuric acid, methanesulfonic acid, p-toluene sulfonic acid, metals or their compounds. Examples of those suitable are tin, titanium, and zirconium, these being used in the form of finely divided metals, or advantageously in the form of their salts, oxides, or soluble organic compounds. Unlike protonic acids, the metal catalysts are high-temperature catalysts whose full activity is often not achieved until temperatures reach above 180°C. However, their use is preferred since the level of formation of by-products, such as olefins from the alcohol used, is lower when comparison is made with protonic catalysis. Examples representing metal catalysts are tin powder, stannous oxide, stannous oxalate, titanium esters, such as tetraisopropyl orthotitanate or tetrabutyl orthotitanate, and zirconium esters, such as tetrabutyl zirconate.

Use may also be made of basic catalysts, such as oxides, hydroxides, hydrogen carbonates, carbonates, or alkoxides of alkali metals or of alkaline earth metals. Among this group, preference is given to use of alkoxides, such as sodium methoxide. It is also possible to prepare alkoxides in situ from an alkali metal and an isononanol mixture or, respectively, a nonanol.

The concentration of catalyst depends on the nature of the catalyst. It is usually from 0.005 to 1.0% by weight, based on the reaction mixture.

The reaction temperatures for transesterification are usually from 100 to 220°C. They have to be at least high enough to permit the alcohol produced from the starting ester to be distilled off from the reaction mixture at the prevailing pressure, mostly atmospheric pressure.

The work-up of the transesterification mixtures may be precisely as described for the esterification mixtures.

The mixtures of the invention, alone or in combination with other plasticizers, may be incorporated in plastics. Preferred plastics are PVC, PVB, homo- and copolymers based on ethylene, propylene, butadiene, vinyl acetate, glycidyl acrylate, glycidyl methacrylate, or acrylates having branched or unbranched alkyl radicals of from 1 to 10 carbon atoms. Other preferred plastics are styrene, acrylonitrile, and homo- or copolymers of cyclic olefins.

Examples which may be mentioned of representatives of the above groups are the following plastics:
polyacrylates having identical or different alkyl radicals having from 4 to 10 carbon atoms bonded to the oxygen atom of the ester group, in particular having the n-butyl, n-hexyl, n-octyl, isononyl, or 2-ethylhexyl radical, polymethacrylate, polymethyl methacrylate, methyl acrylate-butyl acrylate copolymers, methyl methacrylate-butyl methacrylate copolymers, ethylene-vinyl acetate copolymers, chlorinated polyethylene, nitrile rubber, acrylonitrile-butadiene-styrene copolymers, ethylene-propylene copolymers, ethylene-propylene-diene copolymers, styrene-acrylonitrile copolymers, acrylonitrile-butadiene rubber, styrene-butadiene elastomers, methyl methacrylate-styrene-butadiene copolymers, and/or nitrilocellulose.

PVC grades which may be used are suspension, bulk, microsuspension, and preferably emulsion PVC. Besides the esters described of cyclohexanedicarboxylic acid, phthalic acid, adipic acid, and benzoic acid, and besides other plasticizers, there may also be numerous other components known to the skilled worker added to the mixing specification. Examples of these are fillers, pigments, stabilizers, lubricants, blowing agents, kickers, antioxidants, biocides, etc.

The mixtures of the invention are preferably used for producing plastisols, in particular PVC plastisols, with particularly advantageous processing properties. These plastisols may be used in numerous products, such as synthetic leathers, flooring, or wallpapers, etc. Among these applications, particular preference is given to use in cushion vinyl (CV) flooring, and in particular here in the outer layer, where a further improvement is brought about in stain resistance. Use of the mixtures of the invention as a constituent in a mixing specification can give plastisols with low viscosity and increased storage stability together with accelerated gelling and improved low-temperature flexibilization.

It is also possible for the nonylbenzoates or the abovementioned mixtures of the invention with phthalates, with adipates, and/or with cyclohexanedicarboxylates, to be used as flexibilizers in coatings, paints, inks, or, respectively, components of adhesives.

The examples below are intended to illustrate the invention without restricting the scope of application arising from the Description and the Claims.

Example 1:

Preparation of isononyl benzoate

976 g of benzoic acid (8 mol), 1728 g of isononanol from OXENO Olefinchemie GmbH (12 mol), and 0.59 g of butyl titanate (0.06%, based on the amount of acid) are weighed into a four liter distillation flask on top of which a water separator and reflux condenser have been attached, and which has a sampling port and thermometer, and are heated to boiling under nitrogen. The water of reaction produced during the esterification process was removed sequentially. Once the acid value fell below 0.1 mg KOH/g (after about 3 hours), the mixture was first cooled below 60°C, and a 20 cm multifill column was placed on the apparatus. The pressure was then reduced to 2 mbar, and excess alcohol was first distilled off (about 120°C). After removal of an intermediate fraction at up to 140°C it was possible to distill over the isononyl benzoate within a range of 142 to 147°C (at 2 mbar) measured at the head of the column. Purity > 99.7% was determined by gas chromatography.

The dynamic viscosity of the product at 20°C was 8.4 mPa*s.

Example 2:

Preparation of 2-ethylhexyl benzoate (Comparative Example)

Using a method similar to the procedure carried out in Example 1, 12 mol of 2-ethylhexanol were reacted with 8 mol of benzoic acid and tetrabutyl titanate.

Distillation gave 2-ethylhexyl benzoate with purity of 99.7% determined by gas chromatography.

The dynamic viscosity of the product at 20°C was 6.8 mPa*s.

Example 3:

Preparation of 3,5,5-trimethylhexyl benzoate (Comparative Example)

1000 g of 2,4,4-trimethyl-1-pentene (diisobutene) from Oxeno (may be prepared as in DE 10106593.0, for example) were hydroformylated in a 2 l autoclave at 135°C under 270 bar of synthesis gas pressure for 3 hours in the presence of an unmodified rhodium catalyst. The active catalyst was generated in situ from rhodium nonanoate (24.8% by weight of Rh). Rhodium concentration based on diisobutene was set at 20 ppm.

After 3 hours the reaction was terminated and the autoclave was cooled to 20°C.

The reaction discharge comprises 93.5% by weight of 3,5,5-trimethylhexanal, 2.5% by weight of 3,5,5-trimethylhexanol, 3.4% by weight of residual C8 hydrocarbons, and 0.6% by weight of high-boilers.

The reaction discharge was freed from rhodium catalyst by distillation on a laboratory distillation column.

The Rh-free hydroformylation discharge was then hydrogenated in the liquid phase in a fixed-bed reactor in the presence of a Cu/Cr/Ni catalyst at 180°C and 25 bar. After hydrogenation of 3,5,5-trimethylhexanal to give the target product 3,5,5-trimethylhexanol, the hydrogenation discharge was freed from low-boilers (C8 hydrocarbons) by controlled distillation.

The distillation process gave a 3,5,5-trimethylhexanol of purity above 99.5% by weight.

Using a method similar to the procedure carried out under Example 1, **6** mol of the resultant 3,5,5-trimethylhexanol were reacted with **4** mol of benzoic acid and tetrabutyl titanate.

Distillation gave 3,5,5-trimethylhexyl benzoate at 99.7% purity as determined by gas chromatography.

The dynamic viscosity of the product at 20°C was 7.9 mPa*s.

Example 4:

Comparison of volatilities of 2-ethylhexyl benzoate, 3,5,5-trimethylhexyl benzoate, and isononyl benzoate by dynamic TGA measurement

In order to reach conclusions concerning the volatility of the products, the weight losses of the benzoic esters prepared in Examples 1 to 3 were compared by the dynamic TGA method.

To this end, about 40 mg of a specimen were heated under nitrogen in a DuPont*Instrument TGA 951 device in the temperature range from 20 to 300°C, using a dynamic temperature rise of 10 K/min, and the respective weight loss in % was determined.

The table below lists the unevaporated proportions (= 100% - weight loss in %):

*Trade-mark

Table 2:

Temperature in °C	**Isononyl benzoate**	**2-Ethylhexyl benzoate (Comparative Example)**	**3,5,5-Trimethylhexyl benzoate (Comparative Example)**
140	98.5%	98.1%	93.6%
170	93.7%	91.1%	72.9%
200	75.7%	68.2%	9.4%
230	24.2%	12.4%	0%

The temperature at which 50% of the specimen has evaporated is 218°C for the isononyl benzoate of the invention and only 213°C for the comparative specimen 2-ethylhexyl benzoate. In the case of 3,5,5-trimethylhexyl benzoate, the temperature at which 50% of the specimen has evaporated is as low as 184°C.

This provides unambiguous confirmation of the lower volatility of the product prepared according to the invention in relation to the comparative products.

Example 5:

Preparation of plastisols

The fast-gelling plasticizers are represented on their own in mixing specifications 1 to 3, in order to expose more markedly the differences between these grades. Mixing specifications 4-6 comprise industrially relevant mixtures of VESTINOL* 9 (DINP from OXENO Olefinchemie GmbH) with fast-gellers in typical top-coat formulations.

The weight used of the components is found in the table below.

Table 3: Mixing specifications (all data in phr (= parts by weight per 100 parts of PVC))

	1	**2**	**3**	**4**	**5**	**6**
VESTOLIT*B 7021 (Emulsion PVC)	100	100	100	100	100	100
VESTINOL*9 (DINP, *OXENO*)	0	0	0	35	35	35
Isononyl benzoate (from Example 1)	50			15		

*Trade-mark

2-Ethylhexyl benzoate (from Example 2)		50			15	
3,5,5-trimethylhexyl benzoate (from Example 3)			50			15
Drapex* 39 (Costabilizer, *Crompton*)	3	3	3	3	3	3
Mark* CZ 140 (Ca/Zn Stab., *Crompton*)	1.5	1.5	1.5	1.5	1.5	1.5

Prior to addition, the temperature of the plasticizers was controlled to 25°C. The liquid constituents were weighed into a PE beaker first, followed by the pulverulent constituents. The mixture was mixed by stirring with a paste spatula until all the powder had been wetted. The mixing beaker was then clamped into the clamping equipment of a dissolver mixer. Prior to immersing the stirrer into the mixture, the rotation rate was set at 1800 revolutions per minute. After the stirrer had been switched on stirring was continued until the temperature on the digital display of the temperature sensor reached 30.0°C. This ensured that homogenization of the plastisol was achieved with defined energy input. The temperature of the plastisol was then immediately controlled to 25.0°C.

Example 6:

Measurement of plastisol viscosities

The viscosities of the plastisols prepared in Example 5 were measured as follows by a method based on DIN 53 019 using the Physica* DSR 4000 rheometer which is controlled by US 200 software.

The plastisol was again stirred with a spatula in the feed vessel and tested in accordance with the operating instructions in test system Z3 (DIN 25 mm). Measurement proceeded automatically at 25°C by way of the abovementioned software. The settings were as follows:

- Pre-shear of 100 s^{-1} for a period of 60 s, during which no values were measured,
- A downward progression beginning at 200 s^{-1} and ending at 0.1 s^{-1}, divided into a logarithmic series with 30 steps, the duration for each point of measurement being 5 s.

After the test, the test data were processed automatically by the software. Viscosity was plotted as a function of shear rate. Each of the

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measurements was made after 2 h, 24 h, and 7 d. Between these junctures, the paste was stored at 25°C.

The two tables below list these viscosity values obtained after each of the storage times given, for shear rates of 1.06 s^{-1} and 118 s^{-1}.

Table 4: Shear rate 1.06 s^{-1} (viscosity data in Pa*s)

Mixing specification	**1**	**2**	**3**	**4**	**5**	**6**
2 h	**0.71**	0.81	0.60	**1.97**	1.96	1.81
24 h	**0.93**	1.24	0.77	**2.35**	2.41	2.39
7 d	**1.39**	2.63	0.99	**2.93**	3.19	3.04

Table 5: Shear rate 118 s^{-1} (viscosity data in Pa*s)

Mixing specification	**1**	**2**	**3**	**4**	**5**	**6**
2 h	**0.59**	0.61	0.46	**2.50**	2.49	2.14
24 h	**0.73**	0.86	0.57	**2.91**	2.93	2.93
7 d	**1.00**	1.51	0.72	**3.45**	3.60	3.51

The measured values listed in Tables 4 and 5 are intended to show that the viscosity level of the plastisols using the isononyl benzoate of the invention differs only insignificantly from that of the two prior art benzoates. In particular, the three benzoates differ very little in blends with DINP.

Example 7:

Measurement of gelling properties

The gelling performance of the plastisols was tested in a Bohlin* CVO oscillation viscometer (measurement system PP20), operated with shear stress control.

The following parameters were set:

Mode: temperature gradient

start temperature: 25°C
end temperature: 180°C
heating/cooling rate: 2°C/min
temperature after measurement: 25°C
oscillation frequency: 2 Hz
delay time: 1 s
waiting time: 15 s

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continuous oscillation: on
automatic shear stress preset: on
shear stress at start: 0.3 Pa
required deformation: 0.002
gap width 0.5 mm

Test procedure:

A spatula was used to apply a drop of the plastisol to be tested (mixing specifications 1-3 from Example 5), free from air bubbles, to the lower plate of the test system. Care was taken here that some plastisol could exude uniformly out of the measurement system (not more than about 6 mm overall) after the measurement system has been closed. The protective covering, which also serves for thermal insulation, is then superimposed, and the test is started.

The "complex viscosity" of the plastisol was plotted as a function of temperature. The start of gelling is recognizable via a sudden marked rise in complex viscosity. The earlier the onset of this viscosity rise, the better the gelling capability of the system.

Fig. 1 plots that section of the viscosity/temperature curve ("gelling curve") relevant for the onset of gelling (see Fig. 1). The Y axis indicates complex viscosities in Pa•s, and the X axis indicates temperatures in °C . The continuous line denotes plastisol 3 (3,5,5-trimethylhexyl benzoate) and the dotted line denotes plastisol 2 (2-ethylhexyl benzoate), while the dashed line denotes plastisol 1 (isononyl benzoate).

This presentation, which for simplicity only includes the formulations of the fast-gellers without DINP (1-3), shows that the onset of the marked rise in viscosity, i.e. the onset of gelling, is markedly earlier for the isononyl benzoate plastisol than for the corresponding plastisol using 3,5,5-trimethylhexyl benzoate. The somewhat lower gelling temperature for the plastisol based on 2-ethylhexyl benzoate is in agreement with the expectation that gelling temperature will fall with a reduction in chain length. It is surprising here that the effect of the different branching at the same molecular weight is considerably more significantly apparent here than the effect on moving from 2-ethylhexyl benzoate (C8) to isononyl benzoate (C9).

Example 7: Assessment of low-temperature properties via torsional oscillation analysis

The plastisols prepared in Example 5 were spread and gelled to give films of 1 mm thickness in a conventional laboratory gelling oven (Mathis LTSV*) at 200°C for 2 minutes.

Pieces of length 60 mm, width 80 mm, and thickness 1 mm were then stamped out from the films, and stiffness G' and loss modulus G" were determined for each of these at temperatures of from -100 to +100°C, at frequency 1 s^{-1} in MYRENNE ATM* III torsion pendulum equipment to DIN EN ISO 6721 (Part 2).

The glass transition temperature T_G was determined from the maximum of G", and is a measure of flexibility at low temperatures.

The glass transition temperatures of the films produced from plastisols 1-6 from Example 5 can be seen in Table 6:

Table 6:

Plastisol No.	**1**	2	3	**4**	5	6
T_G in °C	**-49**	-47	-39	**-35**	-35	-33

Whereas the glass transition temperatures achievable using isononyl benzoate and 2-ethylhexyl-benzoate, in particular in mixtures, are at a similar level, isononyl benzoate is markedly preferable to 3,5,5-trimethylhexyl benzoate.

In summary it can be stated that, while the viscosity level is practically identical, mixing specifications based on isononyl benzoate have marked advantages in relation to gelling capability, low-temperature flexibilization, and volatility when compared with those based on 3,5,5-trimethylhexyl benzoate.

Particular factors arising from comparison with mixing specifications based on 2-ethylhexyl benzoate give a reduction in volatility and again an improvement in low-temperature flexibilization.

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CLAIMS:

1. A mixture of isomeric isononyl benzoates which, when saponified, produce isononyl alcohols containing less than 10 mol% of 3,5,5-trimethylhexanol.

2. The mixture according to claim 1, wherein the isononyl alcohols are obtained by:

(i) hydroformylating a C_8 olefin mixture obtained by oligomerizing substantially linear butenes, to form a hydroformylation mixture, and

(ii) hydrogenating the hydroformylation mixture.

3. The mixture according to claim 2, wherein the substantially linear butenes have a proportion of isobutene of less than 5% by weight based on a total butene content.

4. The mixture according to claim 3, wherein the proportion of isobutene is less than 1% by weight based on the total butene content.

5. The mixture according to claim 2, 3 or 4, wherein the oligomerization of the substantially linear butenes is conducted on a nickel supported catalyst; the hydroformylation of the C_8 olefin mixture is conducted in the presence of an unmodified cobalt compound; and the hydroformylation mixture is depleted of the cobalt compound prior to the hydrogenation.

6. The mixture according to any one of claims 1 to 5, wherein the mixture of isononyl alcohols contains less than 3% by weight of 3,5,5-trimethylhexanol.

7. A mixture comprising:

(A) from 1 to 99% by weight of a mixture of isomeric isononyl benzoates, where isononyl alcohols obtained by saponifying the benzoates comprise less than 10 mol% of 3,5,5-trimethylhexanol, and

(B) from 99 to 1% by weight of a dialkyl phthalate whose alkyl radical contains from 4 to 13 carbon atoms, wherein the weight percentages are based on a total amount of the ingredients (A) and (B).

8. The mixture as claimed in claim 7, wherein the dialkyl phthalate is diisononyl phthalate.

9. The mixture as claimed in claim 8, wherein isononyl alcohol obtained by saponifying the diisononyl phthalate comprises less than 10 mol% of 3,5,5-trimethylhexanol.

10. The mixture as defined in any one of claims 7 to 9, comprising 10 to 50% by weight of the ingredient (A) and 90 to 50% by weight of the ingredient (B).

11. The mixture as defined in any one of claims 7 to 10, wherein the ingredient (A) is the mixture of isomeric isononyl benzoates as defined in any one of claims 2 to 6.

12. A mixture comprising:

(A) from 1 to 99% by weight of a mixture of isomeric isononyl benzoates, where isononyl alcohols obtained by saponifying the benzoates comprise less than 10 mol% of 3,5,5-trimethylhexanol, and

(C) from 99 to 1% by weight of an alkyl adipate whose alkyl radical contains from 4 to 13 carbon atoms.

13. The mixture as claimed in claim 12, wherein the alkyl adipate is diisononyl adipate.

14. The mixture as claimed in claim 13, wherein isononyl alcohol obtained by saponifying the diisononyl adipate comprises less than 10 mol% of 3,5,5-trimethylhexanol.

15. The mixture as defined in any one of claims 12 to 14, comprising 10 to 50% by weight of the ingredient (A) and 90 to 50% by weight of the ingredient (C).

16. The mixture as defined in any one of claims 12 to 15, wherein the ingredient (A) is the mixture of isomeric isononyl benzoates as defined in any one of claims 2 to 6.

17. A mixture comprising:

(A) from 1 to 99% by weight of a mixture of isomeric isononyl benzoates, where isononyl alcohols obtained by saponifying the benzoates comprise less than 10 mol% of 3,5,5-trimethylhexanol, and

(D) from 99 to 1% by weight of an alkyl cyclohexanedicarboxylate whose alkyl radical contains from 4 to 13 carbon atoms.

18. The mixture as claimed in claim 17, wherein the alkyl cyclohexanedicarboxylate is diisononyl cyclohexanedicarboxylate.

19. The mixture as claimed in claim 18, wherein isononanol obtained by saponifying the diisononyl cyclohexanedicarboxylate comprises less than 10 mol% of 3,5,5-trimethylhexanol.

20. The mixture as defined in any one of claims 17 to 19, comprising 10 to 50% by weight of the ingredient (A) and 90 to 50% by weight of the ingredient (D).

21. The mixture as defined in any one of claims 17 to 20, wherein the ingredient (A) is the mixture of isomeric isononyl benzoates as defined in any one of claims 2 to 6.

22. A process for preparing the mixture of isomeric isononyl benzoates as defined in any one of claims 1 to 6, which comprises esterifying benzoic acid with the mixture of isononyl alcohols.

23. A process for preparing the mixture of isomeric nonyl benzoates as defined in any one of claims 1 to 6, which comprises transesterifying a C_{1-8} alkyl benzoate with the mixture of isononyl alcohols.

24. A plastics composition, comprising:

a plastics material, and

the mixture as defined in any one of claims 1 to 21, as a plasticizer.

25. A polyvinyl chloride composition, comprising:

polyvinyl chloride, and

the mixture as defined in any one of claims 1 to 21, as a plasticizer.

26. A polyvinyl chloride plastisol composition, comprising:

a polyvinyl chloride plastisol, and

the mixture as defined in any one of claims 1 to 21, as a plasticizer.

27. A use of the mixture as claimed in any one of claims 1 to 21 as a plasticizer in plastics.

28. A use of the mixture as claimed in any one of claims 1 to 21 as a plasticizer in polyvinyl chloride.

29. A use of the mixture as claimed in any one of claims 1 to 21 as a plasticizer in a polyvinyl chloride plastisol.

30. A use of the mixture as claimed in any one of claims 1 to 21 in a paint or coating.

31. A use of the mixture as claimed in any one of claims 1 to 21 in an adhesive or a component of an adhesive.

FETHERSTONHAUGH & CO.
OTTAWA, CANADA

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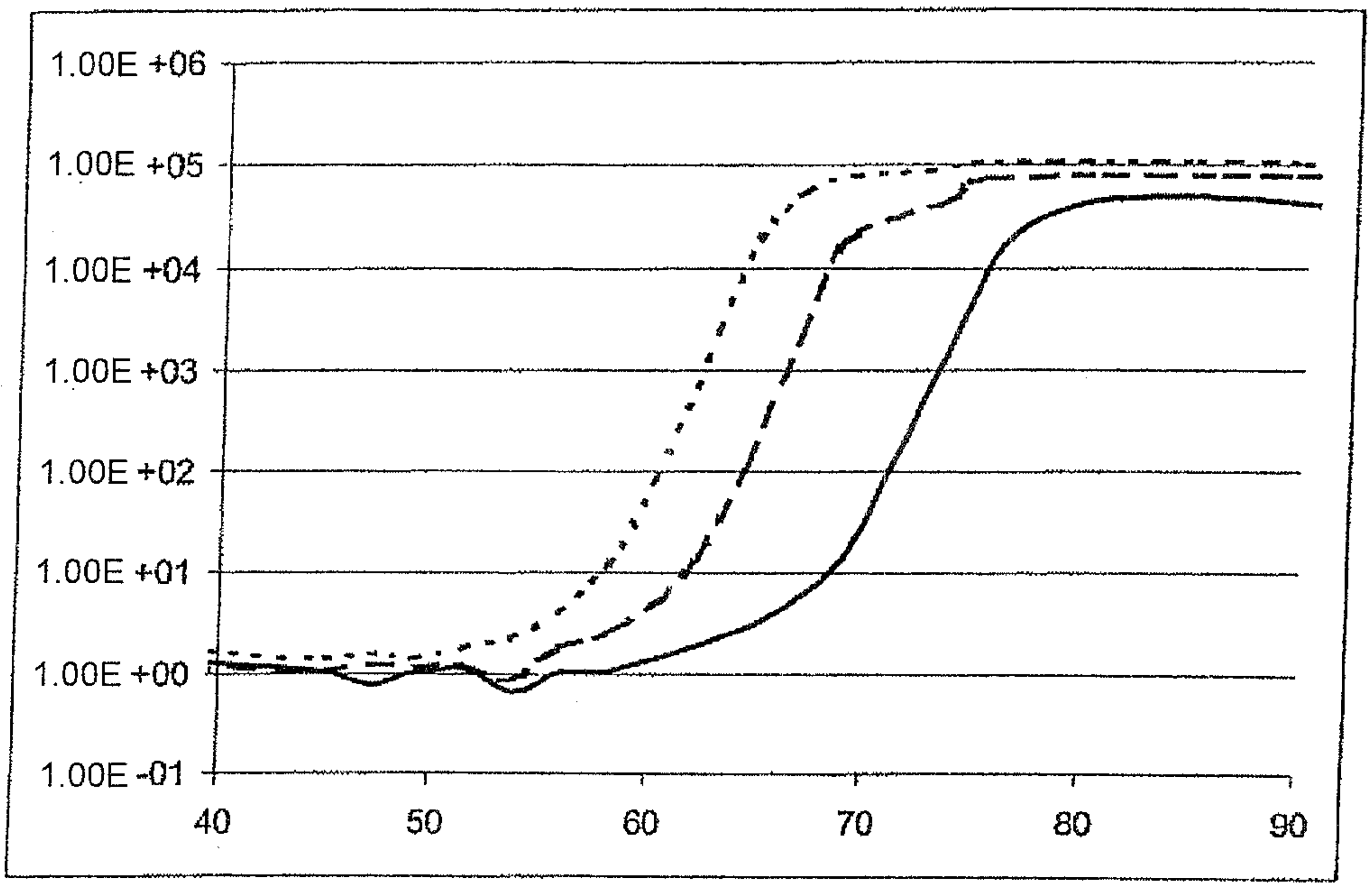

Fig 1: Gelling curves of plastisols 1-3