

In a second aspect, there is provided a composition comprising:

- an ester mixture as defined above,
- a high boiler and/or a low boiler;

wherein a high boiler is a compound with a boiling point above that of the C₁₀, C₁₀-ester, and

wherein a low boiler is a compound with a boiling point below that of the C₈, C₈-ester.

In a third aspect, there is provided a polymer composition comprising:

- an ester mixture as defined above,
- a polymer.

In a fourth aspect, there is provided the use of an ester mixture as defined above as a plasticizer.

In a fifth aspect, there is provided a method comprising the steps of

- a) providing a dianhydrohexitol,
- b) admixing n-octanoic acid and n-decanoic acid,
- c) esterifying the acids of b) with the alcohol of a) in the presence of at least one catalyst,
- d) terminating the esterifying reaction of c) as soon as the proportion of monoester has fallen below 2.0 area%.

C8 or as the case may be C10 refers to the number of carbon atoms in the carbon chain.

The proportion of C10 in the ester mixture computes as the sum of C8 and C10 in the ester mixture (corresponds to 100 mol%) minus the proportion of C8.

For example, a mixture consisting to equal parts of pure C8-diester and pure C10-diester has a 50 mol% proportion of C8. But, for example, a pure C8/C10-ester, i.e. an ester wherein one alcohol group is esterified with C8 and the other alcohol group is esterified with C10, similarly also has a 50 mol% proportion of C8. The latter is also an ester mixture for the purposes of this invention.

"In the entire ester mixture" is to be understood as also comprehending those esters in the ester mixture which do not conform to formula I, for example monoesters of dianhydrohexitol which are present in the ester mixture. Following saponification of the entire ester mixture, all the C8-acids and all the C10-acids are captured separately and ratioed.

Table 1: Feed ratio and product composition of recited isosorbide diesters.

No.	C8 proportion of feed [mol%]	C10 proportion of feed [mol%]	Low boilers [area%]	Diesters [area%]	High boilers [area%]	C8/C10 ratio by GC after saponification [area%]	C8/C10 ratio by GC after saponification [standardized % by mass]	C8/C10 ratio by GC after saponification [standardized mol%]
-	100	0	0.20	98.74	1.05	99.9/0.0	100.0/0.0	100.0/0.0
3*	85	15	0.39	98.90	0.71	79.9/19.8	83.0/17.0	85.4/14.6
4*	75	25	0.26	98.92	0.81	68.0/31.8	72.1/27.9	75.5/24.5
5*	65	35	0.26	99.18	0.52	58.0/42.0	62.6/37.4	66.7/33.3
6*	58	42	0.23	99.08	0.69	48.3/51.5	53.2/46.8	57.6/42.4
7*	57	43	0.18	98.67	1.04	47.9/51.8	52.8/47.2	57.2/42.8
8*	50	50	0.26	99.33	0.40	42.8/56.9	47.6/52.4	52.0/48.0
9	40	60	0.38	99.28	0.34	32.9/66.9	37.3/62.7	41.5/58.5
10	25	75	0.29	99.56	0.14	19.9/79.6	23.2/76.8	26.5/73.5
-	0	100	0.39	99.53	0.08	0.2/99.4	0.0/100	0.0/100.0
11*	57	43	2.2	97.3	0.5	53.0/46.2	58.1/41.9	62.4/37.6
12*	57	43	4.6	95.0	0.4	52.7/46.2	58.0/42.0	62.3/37.7
13*	57	43	0.1	94.8	5.0	53.4/45.2	58.9/41.1	63.1/36.9
14*	57	43	0.3	74.3	25.5	53.8/45.0	59.1/40.9	63.3/36.7

*Polymer compositions according to the invention

Table 3:

paste number	1	2	3*	4*	5*	6*	7*	8*	9	10
paste viscosity after 24 h (100 s ⁻¹)	5.73	10.8	6.32	6.60	6.64	6.68	6.77	6.84	6.99	7.35

*Polymer compositions according to the invention

Comparing the pastes, the pastes formed from the inventive polymer compositions (3, 4, 5, 6, 7, 8) have a significantly lower paste viscosity than the paste comprising ISDIN-IS (paste number 2). Using purely ISDIN-IS (non-inventive polymer composition 2) it is virtually impossible to produce a readily processable PVC paste, since its paste viscosity is very high.

PVC pastes based on an inventive polymer composition versus a similar paste based on an isosorbide ester of isononanoic acid have, irrespective of the shear rate, a lower shear viscosity and hence an improved processability.

3. Gelling behaviour

The gelling behaviour of the pastes was studied in a Physica MCR 101 in oscillation mode using a plate-on-plate measurement system (PP25), operated with shear-stress control. An additional temperature-regulating hood was attached to the equipment in order to homogenize heat distribution and achieve a uniform sample temperature.

The settings for the parameters were as follows:

Mode: temperature gradient
starting temperature: 25°C
final temperature: 180°C
heating/cooling rate: 5°C/min
oscillation frequency: 4-0.1 Hz ramp logarithmic
angular frequency omega: 10 1/s
number of measurement points: 63
measurement-point duration: 0.5 min
automatic gap adjustment F : 0 N
constant measurement-point duration
gap width: 0.5 mm

Measurement procedure:

A spatula was used to apply a drop of the paste to be measured, free from air bubbles, to the lower plate of the measurement system. Care was taken here to ensure that some paste could exude uniformly out of the measurement system (although not more than about 6 mm overall) after the measurement system had been closed. The temperature-regulating hood was then positioned over the specimen and the measurement was started. The so-called complex viscosity of the paste was determined as a function of the temperature. Since a certain temperature is attained within a time span (determined by the heating rate of 5°C/min), information is obtained about the gelling rate of the measured system as well as about its gelling temperature. The onset of the gelling process was discernible in a sudden marked rise in the complex viscosity. The earlier the onset of this viscosity rise, the better the gellability of the system.

The measured curves obtained were used to determine the cross-over temperature. This procedure computes the point of intersection for the two y-variables chosen. The procedure is used to find the end of the linear viscoelastic region in an amplitude sweep (y: G' , G'' ; x: γ) in order to find the crossing frequency in a frequency sweep (y: G' , G'' ; x: frequency) or to ascertain the gel time or cure temperature (y: G' , G'' ; x: time or temperature). The cross-over temperature documented here corresponds to the temperature of the first intersection of G' and G'' .

The results are shown in Table 4. Paste number correlates with the recipe number in Table 2.

Table 4:

paste number	1	2	3*	4*	5*	6*	7*	8*	9	10
cross-over temperature °C	75.4	76.4	70.5	71.2	72.8	73.6	72.7	72.6	74.9	75.8

*Polymer compositions according to the invention

Gelling behaviour:

Compared with the paste which contains ISDIN-IS (paste number 2), the pastes which contain an inventive polymer composition (paste numbers 3 to 8) exhibit significantly faster gelling. The gelling of pastes 3 to 8 is also faster than the gelling of pastes 9 and 10 and also of paste 1, which comprises the existing industry standard DINP.

4. Melting points of purely ester mixtures

Melting points were determined using Differential Scanning Calorimetry (DSC), in each case on the basis of the signal for the onset of melting. In the case of two or more melting points, the highest melting point was reported, since the first crystallizations ensue below this temperature.

The results are shown in Table 5. Plasticizer number correlates with the recipe number in Table 2.

Table 5:

plasticizer number	1	2	3*	4*	5*	6*	7*	8*	9	10
temperature °C	n.d.	n.d.	7	3	3	5	5	7.5	13	22

*Polymer compositions according to the invention

n.d. = not determinable

No melting point could be determined for plasticizer numbers 1 and 2. These substances merely exhibit a glass transition, since they are amorphous.

All melting points above 10°C fail to satisfy the criteria for a plasticizer to be readily employable in large-scale industrial processes, since the products otherwise would have to be excessively heated at cold times of the year, which would lead to very high energy costs in order to ensure adequate flowability. Excessive heating could also induce premature gelling of the pastes even during the mixing operation, combined with a pronounced tendency to thicken, and hence significantly compromised processability.

Isosorbide esters with exclusively C8-acid or C10-acid have a comparatively high melting point and are accordingly economically unviable for plastisol methods (this corresponds to about one third of all commercial applications) for the abovementioned reasons. The C8/C10 mixtures all without exception have lower melting points and are accordingly significantly more suitable.

Avoidance of high boilers

The formation of large proportions of high boilers leads to a significantly comprised performance of the plasticizer, specifically as regards processability (gelling) and efficiency (Shore hardness). To reduce the content level of high boilers in the product mixture, the method

The results are shown in Table 7. Plasticizer number correlates with the recipe number in Table 6.

Table 7:

Plasticizer number	7 [*]	11 [*]	12 [*]	13 [*]	14 [*]
loss of mass [%]	3.50	3.71	4.55	2.69	2.71

*Polymer compositions according to the invention

The polymer composition comprising an ester mixture obtained ~~from by a non-inventive method~~ (plasticizer No. 12) gives a significantly higher loss of mass than polymer compositions comprising an ester mixture obtained ~~from by an inventive method~~ (plasticizer numbers 7, 11, 13).

3. Water resistance

Ageing resistance under various ambient conditions is a further essential quality criterion for PVC plasticizers. Especially the behaviour with regard to water (water imbibition & leachability of recipe constituents) and with regard to elevated temperatures (evaporation of recipe constituents & thermal ageing) offers an insight into ageing resistance.

If a plastic article imbibes water to a major degree, this changes not only the materials properties thereof but also its visual appearance (e.g. haze). High water imbibition is accordingly undesirable in general. Leachability is an additional criterion for setting the durability of formulation constituents under service conditions. This holds particularly for stabilizers, plasticizers and/or constituents thereof, since any reduction in the concentration of these recipe constituents in the plastic article can not only worsen the materials properties but also drastically shorten the useful life.

Water resistance was determined using fully gelled 1 mm polymer films of the corresponding plastisols (gelling conditions in Mathis oven: 200°C/2 min). The test specimens used were roundels 3 cm in diameter cut out of the films. Before being lodged in water, the test specimens were stored in a desiccator containing a drier (KC drying beads from BASF SE) at 25°C for 24 hours. The initial weight was determined with an analytical balance to an accuracy of 0.1 mg. The test specimens were then stored in a shaker bath (of the WNB 22 type with "CDP" Peltier cooling, from Memmert GmbH) filled with completely ion-free water at a temperature of 30°C for 7 days under the water surface with sample holders while being continuously agitated.

After lodgement, the roundels were removed from the water bath, dried off and weighed (= weight after 7 days). The difference from the initial weight was used to compute the water imbibition. After being reweighed, the test specimens were again stored for 24 hours at 25°C in a desiccator containing a drier (KC drying beads) and then once more reweighed (final reweighing = weight after drying). The difference from the initial weight before water lodgement was used to compute the percentage loss of mass due to water lodgement (corresponds to loss by leaching).

The results are shown in Table 8. Test specimen number correlates with the recipe number in Table 6.

Table 8:

test specimen number	7 ₋ [*]	11 ₋ [*]	12 ₋ [*]	13 ₋ [*]	14 ₋ [*]
loss of mass [%]	-0.05	- 0.55	- 1.08	- 0.02	- 0.19

*Polymer compositions according to the invention

The mass lost by test specimen 11 is slightly up compared with the mass lost by test specimen 7, while that of test specimen 12 (having a high low-boiler content) is significantly up.

Significantly increased losses of mass severely limit the utility of plasticizers.

4. Plasticizing effect

Its Shore hardness is a measure of the softness of a test specimen. The further a standardized needle is able to penetrate into the test specimen during a certain period of measurement, the lower the measured value obtained. The plasticizer with the highest efficiency produces the lowest value of Shore hardness for the same amount of plasticizer. Since formulations/recipes are in practice frequently standardized/optimized to a certain Shore hardness, accordingly, very efficient plasticizers make it possible to save a certain proportion in the recipe, and this represents a cost reduction for the processor.

To determine the Shore hardnesses, the pastes obtained as described above were poured into round brass moulds 42 mm in diameter (weight poured into mould: 20.0 g). The pastes in the moulds were then gelled at 200°C in a circulating air drying cabinet for 30 min, removed after

cooling and stored for at least 24 hours in a conditioning cabinet (25°C) before measurement. Disc thickness was about 12 mm.

The hardness measurements were carried out to DIN 53 505 using a Shore A meter from Zwick-Roell, the measured value being read off after 3 seconds in each case. Measurements were carried out at three different places on each test specimen and averaged.

The results are shown in Table 9. Test specimen number correlates with the recipe number in Tables 2 and/or 6.

Table 9:

test specimen number	1	2	3*	4*	5*	6*	7*	8*	9	10
Shore A	80	84	80	81	80	82	82	82	82	83

test specimen number	11*	12*	13*	14*
Shore A	83	82	83	88

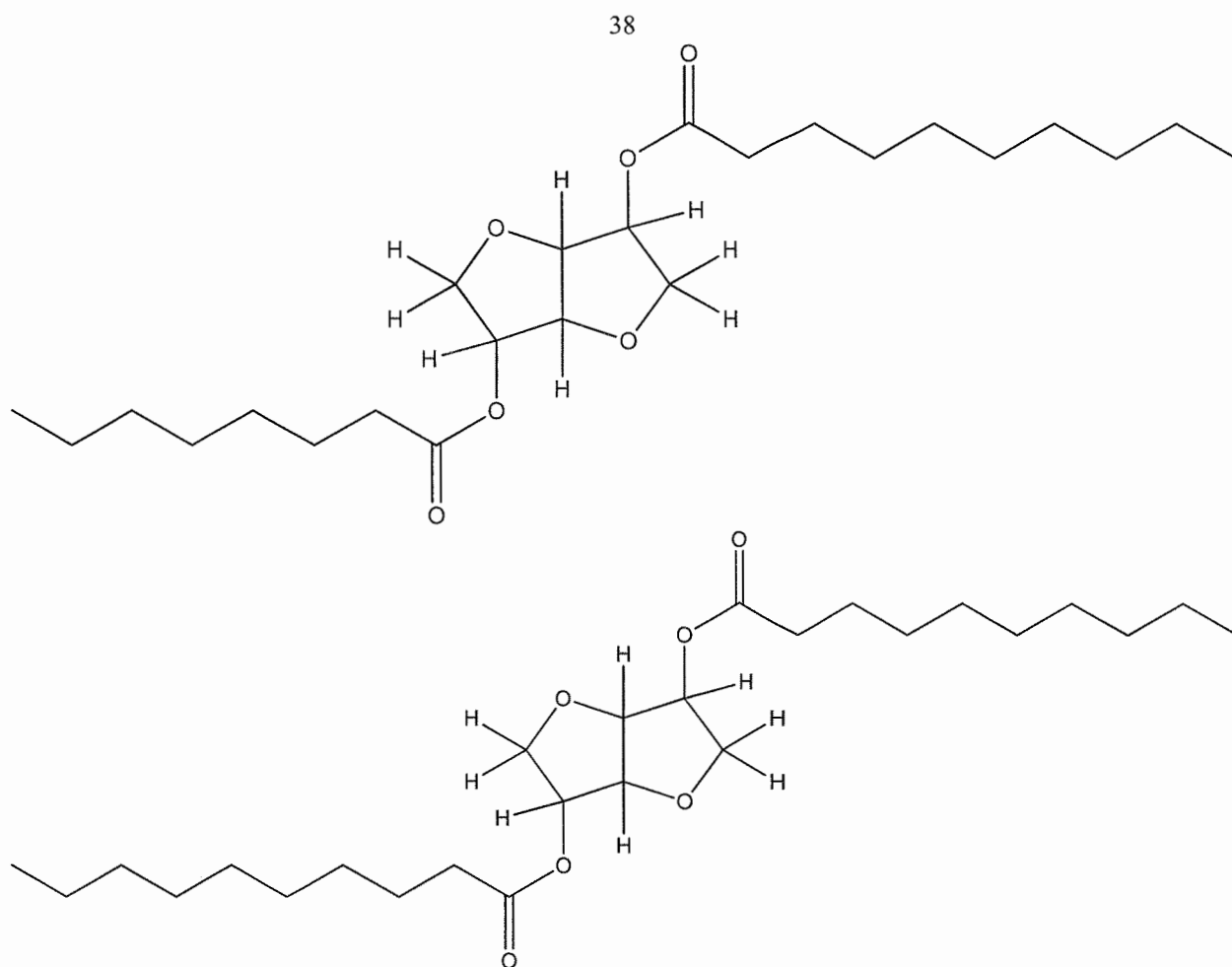
*Polymer compositions according to the invention

Compared with test specimen 2, which contains isosorbide esters based on isononanoic acid (ISDIN-IS) as plasticizer, test specimens 3-10 and 11-13 exhibit a lower Shore A hardness, i.e. greater "softness". The method of the present invention thus delivers ester mixtures that have a better efficiency in PVC mixtures than ISDIN-IS has. Plasticizer can accordingly be thereby saved, which leads to lower recipe costs. Recipe 14, ~~comprising an ester mixture obtained by a non-inventive method,~~ has a significantly higher Shore hardness.

Foams

The invention further claims the use in foams of an ester mixture according to the invention.

Many PVC articles are typically made to include layers of foam in order that the weight of the products and thus also the costs may be reduced by virtue of the lower material requirements. Floorings, wall coverings or artificial leathers are exemplary fields of use here. The user of a



5 8. A composition comprising:

- an ester mixture according to any of Claims 1 to 7,
- a high boiler and/or a low boiler;

wherein a high boiler is a compound with a boiling point above that of the C₁₀, C₁₀-ester,
and wherein a low boiler is a compound with a boiling point below that of the C₈, C₈-
ester.

9. A composition according to Claim 8,

wherein the proportion of high boilers is less than 15 area% based on the ester signals of the composition.

10. A composition according to either of Claims 8 and 9,

wherein the proportion of low boilers is less than 4.5 area% based on the ester signals of the composition.

20 11. A polymer composition comprising: