

PLASTICIZING COMPOSITION

The invention relates to a plasticizing composition comprising a resin of vinyl chloride type and a plasticizing agent which comprises at least one diester derived from a diacid chosen from succinic acid, glutaric acid, adipic acid, ethylsuccinic acid, methylglutaric acid and their mixture. The present invention relates more particularly to a plasticizing agent which comprises at least one diester derived from a diacid chosen from succinic acid, glutaric acid, adipic acid, ethylsuccinic acid, methylglutaric acid and their mixture and to its process of preparation. The present invention also relates to the uses of the plasticizing composition.

Prior art

The plasticizing agents predominantly used are commonly known as "General Purpose" (GP) phthalates and thus represent 88% of consumption worldwide (6.7 MTon in 2011). The GP phthalates family includes DEHP (di(2-ethylhexyl) phthalate), DINP (diisononyl phthalate) and DIDP (diisodecyl phthalate). These three combined phthalates represent of the order of 83% of worldwide demand for plasticizers. DEHP alone represents approximately 50% of worldwide demand.

Aim of the invention

The general aim of the invention is to provide novel plasticizing compositions.

The plasticizing agent according to the invention exhibits a good performance for formulations of different types (foam, film and paste). This plasticizer rapidly gels, has a very low viscosity and ages very well. Efficient debubbling is one of these leading characteristics. The foams prepared with this plasticizer have low densities, a high rate of expansion and excellent qualities.

It is an aim in particular of the invention to provide a process which makes it possible to obtain the plasticizing agent.

The inventors have developed a process for the preparation of diester compounds starting from dinitriles and/or diacids employing a hydrolysis reaction followed by an esterification stage. A decoloration and/or purification stage makes it possible to obtain a pure diester.

5 The invention relates more particularly still to a process for the preparation of branched diester compounds, such as the diester of 2-methylglutaric acid (also known as MGA) and the diester of 2-ethylsuccinic acid (also known as ESA).

The diester based on MGA alone or as a mixture with the diester based on ESA has a promising future in the milieu of the chemical industries. It is a plasticizer having plasticizing properties which can replace plasticizers based on phthalates and devoid of phthalates. It can be used as replacement for plasticizer, all alone or as a mixture with other plasticizers, for preparations/formulations of polyamides, of concrete, of polyesters, of polyurethanes, of vinyl chloride resins, of ethylene/vinyl acetate copolymers, of rubber, of mastics or of their mixtures.

15 The diester is obtained either from dinitriles, involving a diacid intermediate, or from diacid directly.

WO 2007/141404 provides for the preparation of diacid compounds by hydrolysis of dinitrile compounds in the presence of an excess of basic hydroxyl compounds, the carboxylate salt obtained subsequently being reacted with an inorganic acid in order to recover the diacid compound.

WO 2008/062058 provides for the preparation of diacid compounds by hydrolysis of dinitrile compounds in the presence of an excess of strong inorganic acid.

WO2007/101929 provides for the preparation of diester by hydrolysis of dinitriles by the acid route or by the basic route; the diacid intermediate is subsequently esterified in the presence of methanol in order to obtain the corresponding dimethyl ester.

The present invention relates to a plasticizing composition comprising a resin and a plasticizing agent which comprises at least one diester of general formula (I):



derived from a diacid chosen from succinic acid, glutaric acid, adipic acid, ethylsuccinic acid, methylglutaric acid and their mixture,

in which:

- A can be a linear or branched aliphatic chain comprising from 4 to 6 carbons, and

- R can be an alkyl, a cycloalkyl or an aryl;

in particular, R is a substituted or unsubstituted cycloalkyl of 5 to 6 carbon atoms;

or a branched alkyl having from 4 to 10 carbon atoms.

Preferably, R is cyclohexyl or 2-ethylhexyl.

According to one embodiment of the invention, the plasticizing agent comprises a mixture comprising:

from 70% to 95% by weight of methylglutaric acid diester;

from 5% to 30% by weight of ethylsuccinic acid diester;

from 0% to 10% by weight of adipic acid diester.

According to another embodiment of the invention, the plasticizing agent comprises a mixture comprising:

from 95% to 100% by weight of methylglutaric acid diester, and

from 0% to 5% by weight of ethylsuccinic acid diester.

According to a preferred embodiment of the invention, the diester is the dicyclohexyl one of methylglutaric acid (DCH-MGA).

According to another embodiment of the invention, the diester is the diethylhexyl one of adipic acid (DCH-AA).

According to a third embodiment of the invention, the diester is the diethylhexyl one of methylglutaric acid (DEH-MGA).

The plasticizer of this invention can be prepared by esterification of diacids with these cyclic alcohols.

Reactions:

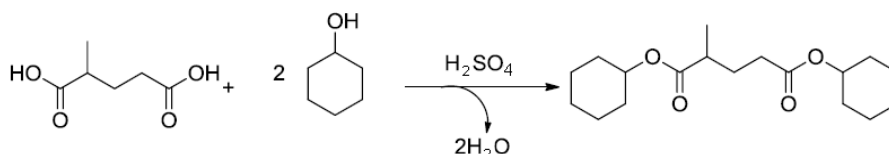
During the hydrolysis reaction of the dinitrile compound in the presence of acid, diacids and ammonium hydrogensulfate salt are formed. The latter can be

recovered in value in the form of ammonium sulfates by its reaction with another molecule of ammonia.

Diagrammatically, the hydrolysis reaction of a dinitrile compound, for example 2-methylglutaronitrile, to give a diacid intermediate compound of the process of the invention can be represented in the following way:



In the reaction medium, the diacid compound is subsequently subjected to an esterification reaction with an alcohol, for example cyclohexanol, to give a diester of the process of the invention in the following way:



Examples

The percentages are given by weight, with respect to the weight of the total composition. The temperatures are given in degrees Celsius (°C).

Example 1

General procedure for the synthesis of plasticizers by esterification.

The catalyst, for example sulfuric acid, is added at 80°C to a 1000 ml jacketed reactor equipped with a system for bleeding at the bottom, with a stirring system, with a nitrogen inlet, with a thermometer, with a Dean and Stark apparatus, with a pump for providing the vacuum and with a dropping funnel equipped with a cooling and heating system, via which the acid and the alcohol, the stoichiometry of which is 1: 2, are added. The reaction takes place at 140°C with removal of the water as the reaction progresses. The stripping with nitrogen thus promotes its removal and its recovery in the Dean and Stark apparatus. Once the amount of water co-produced has been completely collected, the temperature is raised above 140°C and the pressure is lowered in order to remove the excess alcohol. The reaction

medium is subsequently washed several times with sodium chloride solutions and, at the end, with demineralized water. The remaining catalyst is neutralized with sodium carbonate. A stage of decoloration by passing through charcoal can be carried out according to the level of coloration of the medium. The organic phase comprising the diester is subsequently purified and decolored by distillation. The pure and colorless diester is thus obtained with good yields.



Table 1: summary of the diesters prepared by reaction of alcohol and diacids.

Nomenclature	A	R	MW (g/mol)
Bis(2-ethylhexyl) succinate	-(CH ₂) ₂ -	- 2-Ethylhexyl	342
Bis(2-ethylhexyl) glutarate	-(CH ₂) ₃ -	- 2-Ethylhexyl	356
Dicyclohexyl adipate	-(CH ₂) ₄ -	- Cyclohexyl	310
Bis(2-ethylhexyl) 2-methylglutarate	-CH ₂ -CH ₂ -CH(CH ₃)-	- 2-Ethylhexyl	370
Dicyclohexyl 2-methylglutarate	-CH ₂ -CH ₂ -CH(CH ₃)-	- Cyclohexyl	310
Bis(2-ethylhexyl) 2-ethylsuccinate	-CH ₂ -CH(CH ₂ CH ₃)-	- 2-Ethylhexyl	370
Dicyclohexyl 2-ethylsuccinate	-CH ₂ -CH(CH ₂ CH ₃)-	- Cyclohexyl	310
Plast Fast = mixture of 95% dicyclohexyl methylglutarate and 5% dicyclohexyl 2-ethylsuccinate	95%: -CH ₂ -CH ₂ -CH(CH ₃)- 5%: -CH ₂ -CH(CH ₂ CH ₃)-	- Cyclohexyl	310

Synthesis of compounds based on PVC: Plasticization

All the plasticizers used for the tests with the PVC resins under different formulations are summarized in table 2.

Table 2: description of the plasticizers

Plasticizer	Manufacturer	Chemical name	MW (g/mol)
DEHP	Arkema	Di(2-ethylhexyl) phthalate	390
DINP	BASF	Diisononyl phthalate	418
DINCH	BASF	1,2-Cyclohexanedicarboxylic acid, diisononyl ester	425
DOTP	Eastman	Di(2-ethylhexyl) terephthalate	390
Nexo E01	Nexoleum	Methyl epoxy soyate	327
Benzoflex 2088	Eastman	Mixture of benzoate esters (78-80%) and dipropylene glycol dibenzoate (18-20%)	350
Jayflex MB10	Exxon	Isodecyl monobenzoate	262
Plast Fast	Solvay	2-Methylglutarate diester	310

A comparative assessment of the performances of the plasticizers studied was carried out for each formulation. The criteria for classifying the performance of the plasticizers, in comparison with DINP, are classified as follows:

0: idem	-0.5: slightly poorer	0.5: slightly better
	-1: poorer	1: better
	-2: bad	2: excellent
	-3: very bad	3: outstanding

Example 2

Each plasticizer listed in table 2 makes it possible to produce transparent formulations according to table 3 below, using a mixer of medium-speed mixer type at a temperature of 23°C.

Table 3: Recipe for PVC pastes (compact transparent layers):

Starting materials	Amount (phr)
SolVin [®] 382NG	100
Plasticizer	50
Baerostab [®] NT 306 (Ca/Zn)	2.5

The comparison of the data obtained for the formulations synthesized, the plasticizer being modified on each occasion, are summarized in table 4.

Tables 4a to 4i: evaluations and comparison of the properties

4a- Shore A: Hardness (on 6 mm plaques)

Plasticizer	Curings in the oven (cutting)	Pressed films
DEHP	67	75
DINP	72	78
DINCH	74.5	84
DOTP	71	76
Nexo E01	66	70
Plast Fast	65	68
MB10/DINP	68	71
2088/DINP	71	73

4b- Viscosity at low rate gradient ($\text{Eta} = 1.4 \text{ s}^{-1}$)

Plasticizer	t 0	t 0 + 24 h
DEHP	4.4	9.6
DINP	3.6	15.7
DINCH	2.0	3.4
DOTP	3.4	3.4
Nexo E01	2.4	4.0
Plast Fast	2.7	5.9
MB10/DINP	1.6	36.0
2088/DINP	14.4	13.4

5

4c- Relative gelation rate (ARES rheometer, plate-plate, 1 rad/s, temperatures from 23 to 100°C, rise of 3°C/min)

Plasticizers	Gelation
DEHP	0.75
DINP	0
DINCH	-1.5
DOTP	-0.75
Nexo E01	1.25
Plast Fast	2.5
MB10	1
2088	2

4d- Loss in weight (%) at 100°C – ventilated oven

Plasticizer	After 4 days	After 7 days
DEHP	9.85	19.4
DINP	2.3	3.8
DINCH	6.3	10.2
DOTP	3.7	7.55
Nexo E01	12.4	15.8
Plast Fast	20.7	24.6
MB10/DINP	16.4	17.6
2088/DINP	4.7	6.9

4e- Color, gloss and transparency of the PVC films (0.7 mm, 190°C, 2 min)

Plasticizer	Yellowness index	Gloss	Transparency
DEHP	8.4	29.3	83.7
DINP	8.7	30.6	86.5
DINCH	8.1	35.5	85.35
DOTP	7.75	30.05	81.7
Nexo E01	17.8	22.6	74.1
Plast Fast	11.4	29.1	87.9
MB10/DINP	8.0	23.2	82.6
2088/DINP	9.3	25.8	82.4

5

4f- Debubbling

Plasticizer	Column height (ml)	Time (s)
DEHP	98	49.5
DINP	100.5	53
DINCH	100	60.5
DOTP	93	29
Nexo E01	29	23
Plast Fast	94	37
MB10/DINP	83	22
2088/DINP	100	100

4g- Thermal stability (DHC at 180°C and Metrastat at 197°C)

Plasticizer	DHC (min)	Metrastat (min)
DEHP	25	10
DINP	24.2	15
DINCH	28.3	11.6
DOTP	25.8	15.5
Nexo E01	152	27
Plast Fast	27	19.15
MB10/DINP	25.8	19.3
2088/DINP	30.6	18.5

4h- Compatibility plasticizer with PVC ASTM D3291-92

Plasticizer	0	1 Day	1 Week	2 Weeks	4 Weeks	8 Weeks
DINP	0	0	0	0	0	0
Plast Fast	0	0	0	0	0	0

5 4i- Migration of the PVC film (0.7 mm, 190°C, 2 min)

Plasticizer	Migration	Date of manufacture of the film	Comments
DEHP	0	Sept-09	dry sample
DINP	0	Sept-09	dry sample
DINCH	0	Sept-09	dry sample
DOTP	0	Apr-10	dry sample
Nexo E01	-0.5	Apr-10	presence of exudation on the paper
Plast Fast	0	Nov-12	dry sample
MB10/DINP	0	August-10	dry sample
2088/DINP	0	August-10	dry sample

The best performances which emerge for the "Plast Fast" plasticizer are the gelation and the debubbling. This phenomenon is illustrated in figure 1 and the photographs taken for the debubbling are presented in figure 2. In figure 1, it should be understood that the photographs of the 2nd column are taken after 1 minute of resumption of the mixing (that is to say, reincorporation of air). The same applies for the photographs of the 3rd column, after 5 minutes

The classification of the plasticizers according to the grades assigned are summarized in table 5.

Table 5. Summary of the properties obtained with the plasticizers in the transparent PVC paste formulations

Plasticizer	Visco-sity	Aging	Gel-ation	Effi-cacy	Debub-bling	Thermal stability	Color	Transp.	Gloss	Loss in weight	Migra-tion	Score
DEHP	0	0.5	0.75	1	0	-0.125	0	0	0	-2	0	0.125
DINP	0	0	0	0	0	0	0	0	0	0	0	0
DINCH	0.5	1.25	-1.5	-0.75	0	0	0	0	0.75	-1	0	-0.75
DOTP	0	1.25	-0.75	0.25	0	0	0	-0.5	0	-0.75	0	-0.5
Nexo E01	0	1	1.25	1.375	1	3	-1.5	-0.75	-0.5	-1.5	-0.5	2.875
Plast Fast	0.25	0.75	2.5	1.5	0.75	0.25	-0.5	0	0	-2.75	0	2.75
MB10/DINP	0.75	-0.5	1	1.125	-0.5	0.125	0	-0.25	-0.5	-1.75	0	-0.5
2088/DINP	-2	0	2	0.7	-1.5	0.25	-0.25	-0.25	-0.25	-0.5	0	-1.81

5

Example 3

Foam formulations corresponding to table 6 were produced with each plasticizer of table 2 in a mixer of medium-speed type.

10

Table 6: Recipe for PVC pastes – foam-type formulations (expanded layers):

Starting materials	Amount (phr)
SolVin 367NK	100
Plasticizer	62
CaCO ₃ (15 mm)	40
Porofor [®] ADC (50%) + DINP	6
Baerostab [®] KK42 (K/Zn)	2.0

The comparison of the data obtained for the formulations synthesized, the plasticizer being modified on each occasion, are summarized in table 7.

15

Tables 7a and 7b: evaluations and comparison of the properties

7a- Rheology and aging of the paste at low rate gradient ($\text{Eta} = 1.4 \text{ s}^{-1}$)

Plasticizer	t 0	t 0 + 24 h
DEHP	9.1	8.5
DINP	7.2	6.5
DINCH	7.4	5.6
DOTP	10.6	7.5
Nexo E01	3.8	5.0
Plast Fast	11.4	11.7
MB10/DINP	2.1	2.5
2088/DINP	6.9	7.3

7b- Density, color, rate of expansion, and cell quality (thickness 0.35 mm, 2 min at 200°C)

Plasticizer	Density (g/cm ³)	Rate of expansion	Yellowness index	Cell quality
DEHP	0.25	5.1	12.9	Very good
DINP	0.25	5.27	14.19	Very good
DINCH	0.25	5.2	15.2	Very good
DOTP	0.26	5.2	11.25	Very good
Nexo E01	0.24	5.6	47.7	Moderate
Plast Fast	0.21	6.3	19.4	Good
MB10/DINP	0.25	5.4	14	Very good
2088/DINP	0.25	5.2	16.2	Very good

5

The classification of the plasticizers according to the grades assigned are summarized in table 8.

Table 8: Summary of the properties obtained with the plasticizers in the PVC foam formulations

10

Plasticizer	Viscosity	Aging	Color	Density	Rate exp	Cell quality	Score
DEHP	-0.5	0	0.5	0	0	0	0
DINP	0	0	0	0	0	0	0
DINCH	0	0	0	0	0	0	0
DOTP	-0.75	0	0.5	0	0	0	-0.25
Nexo E01	1	0	-2.5	0.5	0.5	-1	-1.5
Plast Fast	-0.75	0	-0.75	1	1.25	-0.5	0.25
MB10/DINP	1.5	0	0	0	0.25	0	1.75
2088/DINP	0	0	0	-0.25	0	0	-0.25

The general comparison of these 2 formulations allows us to have the result of the overall performance of the plasticizers. The mean of the score of the transparent layers and the score of the foam layers gives us the overall performance score for

each plasticizer and thus allows us to compare them. The total score of the performances evaluated is given in table 9.

Table 9. Total score of the performances of each plasticizer.

Plasticizer	Score transparent layers	Score foam layers	Total score
DEHP	0.125	0	0.125
DINP	0	0	0
DINCH	-0.75	0	-0.75
DOTP	-0.5	-0.25	-0.75
Nexo E01	2.875	-1.5	1.38
Plast Fast	2.75	0.25	3
MB10/DINP	-0.5	1.75	1.25
2088/DINP	-1.8125	-0.25	-2.06

5

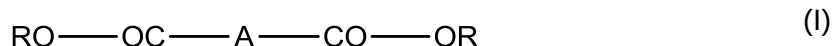
On average, the Plast Fast exhibits a good performance for the 2 recipes tested; it has the highest score in comparison with the other plasticizers. This plasticizer rapidly gels, has a very low viscosity and ages very well. Efficient debubbling is one of these leading characteristics. The foams prepared with this plasticizer have low densities, a high rate of expansion and excellent qualities.

10

CLAIMS

1.- A plasticizing composition comprising a resin of vinyl chloride type and a plasticizing agent which comprises at least one diester of general formula (I):

5



derived from a diacid chosen from succinic acid, glutaric acid, adipic acid, ethylsuccinic acid, methylglutaric acid and their mixture,

10 in which:

- A is a linear or branched C₄ to C₆ aliphatic chain, and
- R is an alkyl, a cycloalkyl or an aryl.

2.- The composition as claimed in claim 1, characterized in that R is a substituted or unsubstituted cycloalkyl of 5 to 6 carbon atoms chosen from cyclopentyl or cyclohexyl or an aryl chosen from benzyl, phenyl, and their isomers.

3.- The composition as claimed in claim 1, characterized in that R is a branched or unbranched alkyl having from 4 to 10 carbon atoms chosen in particular from n-butyl, t-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, ethylhexyl, isooctyl, n-nonyl, isononyl, n-decyl or isodecyl.

4.- The composition as claimed in any one of the preceding claims, characterized in that the plasticizing agent is a mixture of:

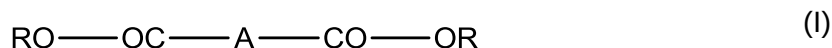
- 25
- from 70% to 95% by weight of methylglutaric acid diester,
 - from 5% to 30% by weight of ethylsuccinic acid diester, and
 - from 0% to 10% by weight of adipic acid diester.

5.- The composition as claimed in any one of claims 1 to 4, characterized in that the plasticizing agent is a mixture of:

- 30
- from 95% to 100% by weight of methylglutaric acid diester, and
 - from 0% to 5% by weight of ethylsuccinic acid diester.

6.- The composition as claimed in any one of the preceding claims, characterized in that the plasticizing agent additionally comprises one or more compounds chosen from phthalate, adipate, benzoate, triglyceride or other polymers.

- 5 7.- A process for the production of a diester or a mixture of diesters of general formula (I):



in which:

- 10 - A is a linear or branched C₄ to C₆ aliphatic chain, and
 - R is an alkyl, a cycloalkyl or an aryl,

characterized in that it comprises the following stages:

- 15 - hydrolysis of a dinitrile or a mixture of dinitriles chosen from adiponitrile, methylglutaronitrile, ethylsuccinonitrile, glutaronitrile or succinonitrile,
 - esterification of a diacid intermediate or of the mixture in the presence of an alcohol,
 - decoloration and purification, making it possible to obtain the corresponding diester or mixture of diesters.

- 20 8.- The process as claimed in claim 7, characterized in that it is produced from a diacid or a mixture of diacids chosen from succinic acid, glutaric acid, adipic acid, ethylsuccinic acid or methylglutaric acid.

- 25 9.- The use of the composition as claimed in any one of claims 1 to 6, for preparing articles selected from toys, films, sheets, flexible pipes, coatings, cables, floor tiles, in particular vinyl-based ones, synthetic leather, adhesives and inks.

10.- The use of the composition as claimed in any one of claims 1 to 6, for the preparation of articles by dry blending or extrusion processes.

30

11.- The use of the composition as claimed in any one of claims 1 to 6, for the preparation of plastisols of paste, film or foam type.