Patent alert April 2025

Phthalate-free plasticizers for PVC

Phthalic acid diesters, commonly known as *phthalates,* are widely used as plasticizers in PVC. These phthalates have been recently under scrutiny for the potential health risks associated with their use such as their interference with human (especially children) hormonal systems. In particular, bis(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and diisobutyl phthalate (DIBP) are classified in REACH[1] as toxic substances for reproduction. This month's selection highlights phthalate-free plasticizers starting with an example showing that replacing phthalate plasticizers might require a mixture of different plasticizers to meet the performance requirements dictated by the targeted application.

This month's selection in brief

[1] https://echa.europa.eu/hot-topics/phthalates

Blood storage containers made of polyvinyl chloride and mixed plasticizers

Patent number: EP3744775

Publication date: 2020-12-02

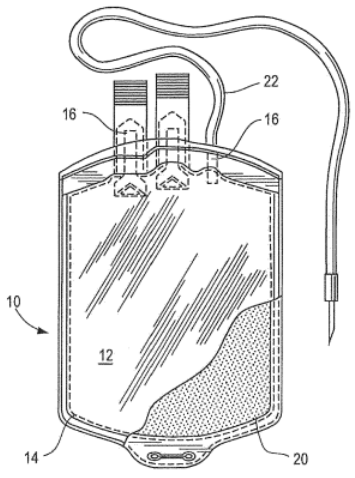
Applicant(s): FENWAL INC.

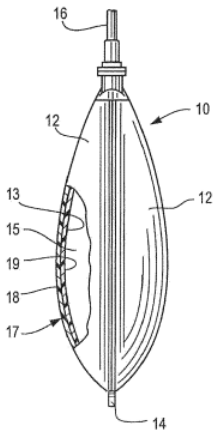
Inventor(s): SANDFORD CRAIG L

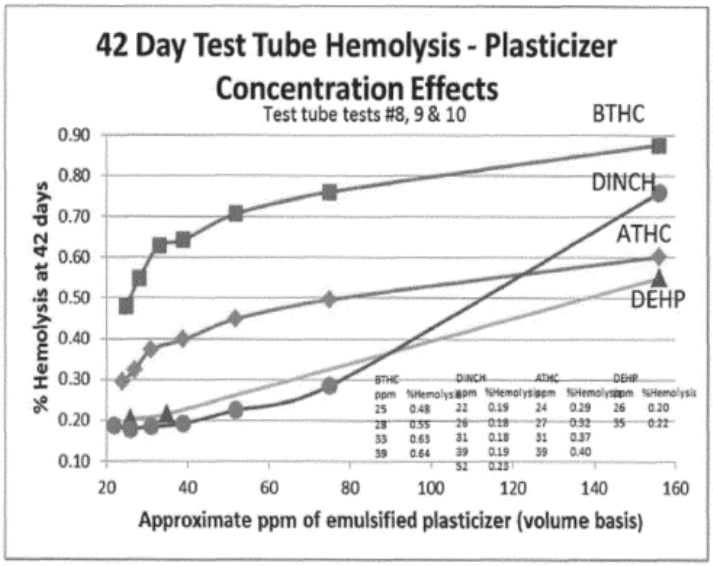
Summary

One example of a currently known and used plasticizer for medical grade PVC is di-ethylhexyl phthalate ester or DEHP. While DEHP plasticized containers have worked well for the storage of red cells, the use of other container materials that assist in providing a suitable storage environment for red blood cells remains a topic of keen interest. The present disclosure is directed to polymeric compositions useful in the manufacture of containers for the storage of blood components. The polymeric compositions include two or more primary plasticizers in a mixture that provides a controlled leaching of the plasticizers from the container wall surface and suppresses the hemolysis of red blood cells. Different mixed primary plasticizer systems may be used in the polymeric composition and the containers made therefrom.

Ideally, the mixture of plasticizers may have a leaching rate and an anti-hemolytic effect comparable to DEHP -- the best known and currently most widely used plasticizer in blood bag applications. DEHP (di-2-ethylhexylphthalate) is the diester of phthalic acid and the branched-chain 2-ethylhexanol. Polymeric compositions made from PVC plasticized with DEHP as the primary plasticizer provide hemolysis suppression at low leaching levels.







Blends of dibenzoate plasticizers

Patent number: EP2658728

Publication date: 2013-11-06

Applicant(s): LANXESS

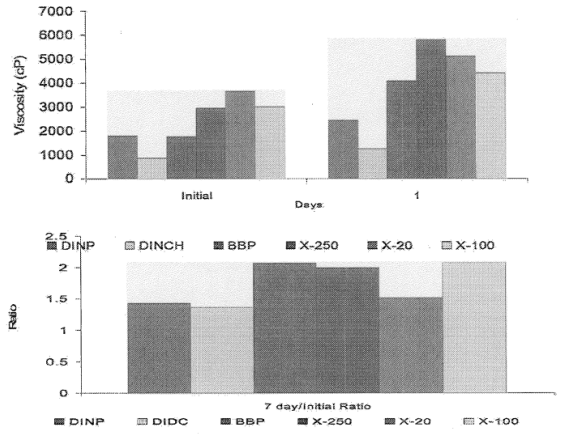
Inventor(s): ARENDT WILLIAM D; MCBRIDE EMILY

Summary

Benzoate ester plasticizers have also been developed as specialty type plasticizers. Benzoate plasticizers have been recognized since the 1940's as useful plasticizers for PVC applications, and subsequently some of these benzoate plasticizers were commercialized. Benzoate plasticizers are well established and have now been in use in PVC applications for decades. By their nature, benzoate plasticizers are non-phthalates; however, they were not created nor specifically established on that basis and were in use well before the demand for phthalate alternatives began. Benzoate plasticizers include monobenzoates and dibenzoates, among others.

Plasticizer blends of the present invention comprise unique blends of three dibenzoate esters: diethylene glycol dibenzoate (DEGDB), dipropylene glycol dibenzoate (DPGDB), and 1,2-propylene glycol dibenzoate (PGDB). These plasticizers are compatible with each other and with various polymers such as elastomers, thermoplastics, and thermosets; such as, for example, polyvinyl chloride and copolymers thereof; various polyurethanes and copolymers thereof; various polyacrylates and copolymers thereof; various polysulfides and copolymers thereof; various epoxies and copolymers thereof; and vinyl acetate and copolymers thereof. The inventive plasticizer triblend functions in PVC applications as a high solvator, but with unexpectedly lower viscosity and improved rheology characteristics than would be expected based upon the individual triblend components alone.

Plasticizer	Initial Inflection	G' Maximum		G' x G"
	Temp (°C)	Temp (°C)	Modulus (Pa)	Temp (°C)
DINP	79	125	3.5×10^5	177
DIDC	107	139	2.8×10^5	181
BBP	61	86	1.1×10^6	167
X-250 diblend tailored to PVC industry (not inventive)	59	91	1.0×10^6	168
X-20 inventive triblend	58	87	1.2×10^6	168
X-100 propylene glycol dibenzoate	59	82	1.2×10^6	164



Acetylated polyglycerine fatty acid ester and a pvc insulator plasticised therewith

Patent number: EP2470596

Publication date: 2012-07-04

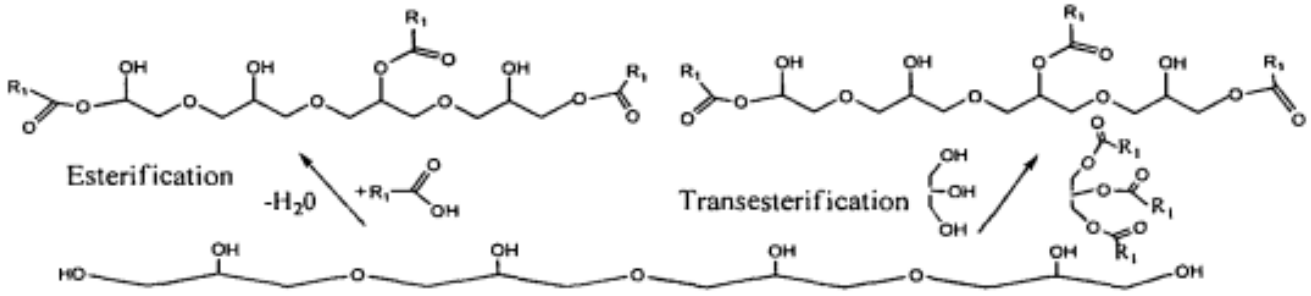
Applicant(s): DOW GLOBAL TECHNOLOGIES LLC

Inventor(s): CHAUDHARY BHARAT I; SCZEKALLA BEATE; SCHILLER KLAUS; MEERBOTE MICHAEL

Summary

The present disclosure addresses the need for phthalate-free plasticized polymers that have the same, or substantially the same, chemical, mechanical, and/or physical properties as polymers containing phthalate plasticizers. The invention is directed to acetylated polyglyceride fatty acid esters and compositions containing the same. A nonlimiting beneficial application for the acetylated polyglyceride fatty acid ester is as a plasticizer. The acetylated fatty acid ester includes a polyglyceride with at least one fatty acid component having from 4 to 22 carbon atoms, the fatty acid components having no hydroxyl groups. The acetylated polyglyceride fatty acid ester also includes at least one acetyl group. The polymeric composition includes a polymeric resin and a plasticizer composition. The plasticizer composition includes an acetylated polyglyceride fatty acid ester and optionally other plasticizers including, but not limited to, an epoxidized fatty acid ester.

Advantages of the present disclosure include (1) a phthalate-free plasticizer with low, or no, adverse health risk to humans; (2) an environmentally safe plasticizer for polymer resins; (3) a phthalate-free plasticizer which provides the same, or substantially the same, properties to a polymer resin as the same polymer resin containing a phthalate-containing plasticizer; and (4) a coating for wire and cable that is phthalate-free.



Method for the preparation of 1,4-cyclohexane dicarboxylic acid dialkyl esters

Patent number: EP3945087

Publication date: 2022-02-02

Applicant(s): EVONIK OPERATIONS GMBH

Inventor(s): KRAFT JOHANNES; ALTMANN LENA; ANTON JOHAN; SCHNEIDER THOMAS

Summary

It is an object of the present invention to provide a process for preparing 1,4-cyclohexanedialkyldicarboxylic esters by means of which the hydrogenation rate can be kept at a higher level and thus the productivity of the hydrogenation process can be increased. The process according to the invention is accordingly a process for the preparation of dialkyl 1,4-cyclohexanedicarboxylates in which the two alkyl groups each have at least 2 carbon atoms, preferably at least 4 carbon atoms, the process comprising at least the nuclear hydrogenation of a dialkyl terephthalate such as diisononyl terephthalate (DINT) in which the two alkyl groups each have at least 2 carbon atoms, preferably at least 4 carbon atoms, with a hydrogen-containing gas to give the corresponding dialkyl 1,4-cyclohexanedicarboxylate, wherein the dialkyl terephthalate used in the nuclear hydrogenation has a carbonyl number (CO) of less than 0.3 mg KOH/g, preferably less than 0.2 mg KOH/g, particularly preferably less than 0.1 mg KOH/g.

The dialkyl 1,4-cyclohexanedicarboxylates prepared according to the invention, in which the two alkyl groups each have at least 2 carbon atoms, preferably at least 4 carbon atoms, it is possible to use advantageously as plasticizer or part of a plasticizer composition in plastics or plastics compositions, as additive in paints or coatings, in adhesives or adhesive components, in sealants or as solvent. The plastics compositions which may comprise the dialkyl 1,4-cyclohexanedicarboxylates prepared may preferably comprise polyvinyl chloride (PVC). As PVC type, the plastic composition preferably contains suspension bulk PVC, microsuspension PVC or emulsion PVC.

Concentration of DINT as a function of time during the hydrogenation

Sample	CO value	c (DINT)* 0 h	c (DINT) 2 h	c (DINT) 4 h	c (DINT) 8 h	c (DINT) 12 h
DINT-1	0.03	100	66.3	40.5	10.6	1.6
DINT-2	0.06	100	71.1	47.3	16.3	3.7
DINT-3	0.07	100	71.9	49.1	17.0	3.5
DINT-4	0.21	100	76.3	57.1	27.3	9.6
DINT-5	0.43	100	80.3	64.0	36.5	17.2
DINT-6	0.57	100	87.9	75.9	53.7	34.9

*the concentration c (DINT) is normalized to 100%.

Undercoating and articles of manufacture coated therewith

Patent number: EP3728483

Publication date: 2020-10-28

Applicant(s): HENKEL

Inventor(s): GUPTA PRIYA; KUMAR GIRDHARI

Summary

In accordance with a first aspect of the invention there is provided a method of forming a coated article, said method comprising:

1) applying an undercoating composition comprising: **(a)** from 20 to 40 wt.-% of a vinyl chloride-vinyl acetate copolymer obtained by polymerization of a co-monomer mixture comprising, based on the total weight of the co-monomers, from 85 to 98 wt.% of vinyl chloride, from 2 to 10 wt.% of vinyl acetate and from 0 to 5 % by weight of a co-monomer selected from C2 to C8 olefins, vinylidene chloride and styrene; **(b)** at least 2 wt.% of plasticizer selected from epoxidized natural oil, preferably epoxidized soybean oil; and **(c)** at least 2 wt.% of at least one aliphatic, cycloaliphatic or aromatic compound having a blocked isocyanate group, wherein said isocyanate group is blocked with a blocking agent capable of de-blocking at a temperature in the range of +/- 20°C compared to the de-blocking temperature of the corresponding isocyanate being blocked with nonylphenol, to at least one surface of said article;

2) applying at least one further coating composition onto said undercoating composition; and

3) curing said undercoating and said at least one further coating composition,

wherein the undercoating composition is in an uncured state upon application of the coating composition immediately contacting it.

Raw Material	Function	Comparative Example 1	Comparative Example 2	Example 1
Vestolit P 1353 K	PVC Resin	13	4.32	-
PCH-72	Copolymer Resin	8	34.52	5
PBM-6	Copolymer Resin	6	-	-
Lacovyl PA 1384	Plastisol Copolymer	-	-	24.4
Diisononyl phthalate	Plasticizer	31.8	30.87	19.27
ESO	Plasticizer		-	5.5
Exxsol D80	Solvent	6	6	5
Ibero-Tec 3017	Adhesion Promoter	-	0.89	-
Ibero-Tec 3157	Adhesion Promoter	0.8	0.51	-
Desmodur BL 3175	Adhesion Promoter	0.6	0.93	-
Nourybond 289	Adhesion Promoter	-	-	6.8
EH 4358S	Hardener	-	-	0.7
Titanium dioxide	Pigment	2	2	
Carbon black paste	Pigment	0.02	0.02	0.02
Calcium Carbonate & Silica	Filler	30.4	18.51	30.66
Zinc & Calcium Oxide	Adjuvants	1.3	1.43	2.49

Vinyl chloride resin plasticizing agent, vinyl chloride resin composition, and molded article thereof

Patent number: EP4116373

Publication date: 2023-01-11

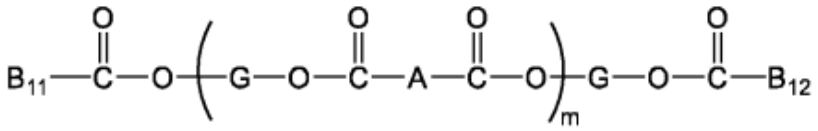
Applicant(s): DIC Corporation

Inventor(s): YAMASAKI MASARU; NOGUCHI TAKAFUMI; TOKORO HIROKI

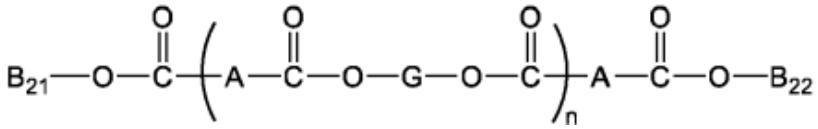
Summary

The present invention is directed at a plasticizer for vinyl chloride resin, wherein the plasticizer is a polyester represented by the following formula (1) or (2) wherein:

- **B11** represents an aliphatic monocarboxylic acid residue having 7 to 20 carbon atoms,
- **B12** represents an aliphatic monocarboxylic acid residue having 7 to 20 carbon atoms,
- **B21** represents an aliphatic monoalcohol residue having 6 to 10 carbon atoms,
- **B22** represents an aliphatic monoalcohol residue having 6 to 10 carbon atoms,
- **G** represents an alkylene glycol residue having 3 to 10 carbon atoms or an oxyalkylene glycol residue having 3 to 10 carbon atoms, **G**'s are the same or different;
- **A** represents an alkylenedicarboxylic acid residue having 6 to 12 carbon atoms, **A**'s are the same or different; and
- each of **m** and **n** represents the number of repeating units in parentheses, and each of **m** and **n** is independently an integer of 1 or more.



(1)



(2)

By the present invention, a plasticizer can be provided which can impart excellent heat resistance to a molded article of a vinyl chloride resin composition, and which has such excellent nonmigratory properties that the plasticizer does not migrate from the molded article to other things.

Plasticizer composition comprising cyclohexane 1,4-diester-based compound, and resin composition comprising same

Patent number: EP3530690

Publication date: 2019-08-28

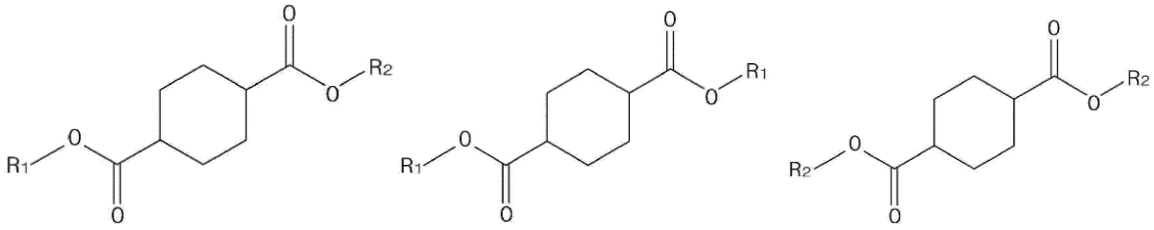
Applicant(s): LG CHEMICAL LTD

Inventor(s): KIM HYUN KYU; LEE MI YEON; JEONG SEOK HO; CHO YUN KI; MOON JEONG JU; KIM JOO HO

Summary

It is an object of the present invention to provide a plasticizer composition including, as a novel compound(s), one or more cyclohexane 1,4-diester-based compounds hydrogenated from one or more terephthalate-based compositions. It is another object of the present invention to provide a resin product in which migration resistance, plasticization efficiency, stress resistance, and the like are improved in a way that mechanical properties such as tensile strength and elongation rate are not sacrificed, by using the plasticizer composition including a cyclohexane 1,4-diester-based compound(s).

According to an embodiment of the present invention, there is provided a plasticizer composition which includes cyclohexane 1,4-diester-based compound represented by the following three chemical formula's where R1 is a butyl group or an isobutyl group, and R2 is a 2-ethylhexyl group.:



A plasticizer composition prepared through trans-esterification and hydrogenation according to an embodiment of the present invention can impart excellent properties in terms of tensile strength, elongation rate, migration resistance, volatile resistance, and the like and provide a resin product having excellent stress resistance, when used for a resin composition.

Plasticizer for vinyl chloride resin containing non-phthalate ester and vinyl chloride resin composition containing such plasticizer

Patent number: EP3124540

Publication date: 2017-02-01

Applicant(s): NEW JAPAN CHEM CO LTD

Inventor(s): MIYAZAKI KEN-ICHI; INOUE TAKAHIRO; TSUJI TAIKI; SATO YUKA; KISHIMOTO MASAFUMI; MIKI SHIGEO

Summary

The present invention relates to a plasticizer for vinyl chloride-based resin containing non-phthalate ester, and a vinyl chloride-based resin composition and the like containing the plasticizer. The inventors of the present invention conducted extensive research in light of these current circumstances and found that an ester obtained by reacting a specific carboxylic acid or a derivative thereof with a specific saturated aliphatic alcohol has superior cold resistance and heat resistance, as well as desirable flexibility, and that, by incorporating this ester to a vinyl chloride-based resin as a plasticizer, it is possible to obtain a vinyl chloride-based resin composition with superior cold resistance and heat resistance, as well as desirable flexibility.

The plasticizer for vinyl chloride-based resin of the present invention is a plasticizer for vinyl chloride-based resin comprising non-phthalate ester (C) obtained by reacting polycarboxylic acid (A) and alcohol (B) wherein:

- the polycarboxylic acid (A) is an alicyclic dicarboxylic acid or a derivative thereof;
- the alcohol (B) is a saturated aliphatic alcohol (B1) comprising a C9 saturated aliphatic alcohol as a major component;
- the saturated aliphatic alcohol (B1) contains a linear C9 saturated aliphatic alcohol (B1-1) of 60 wt% to 95 wt%, and a branched C9 saturated aliphatic alcohol (B1-2) of 5 wt% to 40 wt%;
- the linear-chain ratio of the alcohol (B1) is 60% or more; and
- the non-phthalate ester (C) does not substantially contain a phthalate ester obtained by reacting a phthalic acid compound or a derivative thereof with an alkyl alcohol having 8 or fewer carbon atoms.

The medical vinyl chloride-based resin composition of the present invention has superior cold resistance, superior heat resistance, and desirable flexibility, and does not suffer discoloration after a sterilization or disinfection treatment using ultraviolet or radial rays. Therefore, the medical vinyl chloride-based resin composition of the present invention is superior in ultraviolet resistance and radial ray resistance.

Table 5	Examination Item	Unit (Condition)	Example	Comparative Example			
			E-1	E-1	E-2	E-3	E-4
Plasticizer	Type		Ester E1	Ester E2	Ester E3	DINCH	DOP
	Linear-Chain Ratio of Raw-Material Alcohol (%)		87	0	10	10	0
Tensile Characteristics	100% Modulus	MPa	9	8.5	9.4	10.1	9.4
	Strength	Mpa	20.9	20.5	21.6	22. 7	21.4
	Elongation	%	371	362	374	362	331
Cold Resistance	Softening Temperature	°C	-42	-32	-33	-30	-24