

## **Citroflex**<sup>®</sup> Citric Acid Esters



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# Contents

<b>Citroflex Citric Acid Esters</b>	<b>1</b>
<b>Properties</b>	<b>3</b>
<b>Table 1: Properties and Specifications</b>	<b>4</b>
<b>Resin Compatibility</b>	<b>5</b>
<b>Table 2: Resin Compatibility</b>	<b>6</b>
<b>Performance Testing of Plasticizers</b>	<b>7</b>
<b>Table 3: Characteristics</b>	<b>7</b>
<b>Specific Applications of the Citroflex Esters</b>	<b>8</b>
<b>Table 4: Applications</b>	<b>9</b>
<b>Regulatory/Approval Status of Citroflex Esters</b>	<b>10</b>
<b>Table 5: CFR Listings</b>	<b>11</b>
<b>Literature and Samples</b>	<b>13</b>

## Citroflex® Citric Acid Esters

**Citroflex** citric acid esters provide a wide range of benefits when used as plasticizers with aqueous- and solvent-based polymers, including acrylic, methacrylic, ethyl cellulose, hydroxypropyl methyl cellulose, nitrocellulose, vinyl acetate, vinyl chloride, vinyl pyrrolidone, vinylidene chloride, and urethane polymer systems. Vertellus Specialties Inc. offers both hydrophilic and lipophilic Citroflex esters, allowing the formulator to control the characteristics of polymer systems to suit the needs of the finished product. A partial list of resins and their compatibility with the various Citroflex esters is given in the section of this bulletin on resin compatibility and in Table 2.

Citric acid has a long history of use in food and beverage flavoring. The citric acid esters have a similar history as plasticizers and lubricants in food contact products. This use is reflected in the Regulatory / Approval Status section of this bulletin, including 21 CFR listings, Kosher Certification, and EEC Directive 90/128 listing for food films. Drug Master Files have been submitted for all the Citroflex esters, while Triethyl Citrate NF Grade is the subject of a USP/NF Monograph. Citroflex A-4 (ATBC) is the subject of a Device Master File.

The Citroflex esters offer the formulator a unique combination of environmentally friendly, desirable features. They are not volatile organic compounds (VOC's), yet combine powerful solvency with a low order of toxicity, low volatility, high flash points, and rapid biodegradability. Descriptions, product information, physical properties, and specifications of the Citroflex ester plasticizers are provided in the Properties section of this bulletin.

While the primary use of Citroflex esters is as plasticizers for various polymers, they have proved useful in many other applications. A partial list of these applications is shown in Table 4.

### High Molecular Weight Citroflex Esters

The higher molecular weight citric acid esters (Citroflex® A-4, A-6, and B-6) are effective replacements for di-(2-ethylhexyl) phthalate (DEHP) and di-(2-ethylhexyl) adipate (DEHA). Tables 3, 4, and 5 show their comparative effects on key ambient and low temperature properties of plasticized PVC. Detailed information on these esters and their applications is presented in Vertellus Specialties Inc. Technical Bulletin 103, "Medical Grade Citroflex® Plasticizers."

### Low Molecular Weight Citroflex Esters

The lower molecular weight citric acid esters (Citroflex C-2, A-2, C-4, and A-4) have plasticization characteristics similar to those of the lower molecular weight phthalates, adipates, and sebacates in a variety of polymers. Detailed information on their use in pharmaceutical coatings is presented in a series of monographs offered as Technical Bulletins numbered 102 through 102-5. These bulletins as well as samples of Citroflex products may be obtained by writing Vertellus Specialties Inc., calling Customer Service +1 (336) 292-1781 or at any Vertellus Specialties Inc. sales office or online at [www.vertellus.com](http://www.vertellus.com)

# Citroflex® Citric Acid Esters

## Environmental/Safety

Many studies have been published concerning the citrate plasticizers, their environmental effects, and their uses beginning in 1942 through the present. A partial list of such reports is presented in the reference section of this bulletin. Summary information on biodegradability and toxicology is presented below.

## Biodegradability

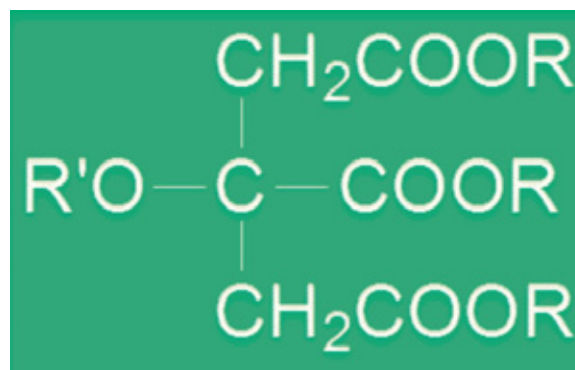
A series of tests were run to determine the biodegradability of the Citroflex esters in comparison with cellulose in standard soil. The cumulative net production of CO<sup>2</sup>-C was compared with the theoretical CO<sup>2</sup>-C

produced in complete reaction of all carbon (C) present for each ester over a 45 day period. This was considered indicative of the biodegradability of the ester. The biodegradability of cellulose was used as standard, and the relative biodegradability of the Citroflex esters was compared to this standard. In all cases, the relative biodegradation index indicated that the Citroflex esters were more highly mineralized than the cellulose reference material.

Based on these tests, both the acetylated and non-acetylated Citroflex esters are readily biodegraded by microorganisms in soil.

## Properties of Citroflex® Esters

Vertellus Specialties Inc. offers several plasticizers under the Citroflex brand name for use in both water-based and solvent-based polymer systems. The generic formula for Citroflex esters and their properties is:



Citroflex	Generic Name	Abbr.	R'	R
<b>C-2</b>	Triethyl Citrate	TEC	H	Ethyl
<b>A-2</b>	Acetyltriethyl Citrate	ATEC	OAc	Ethyl
<b>C-4</b>	Tri-n-butyl Citrate	TBC	H	n-Butyl
<b>A-4</b>	Acetyltri-n-butyl Citrate	ATBC	OAc	n-Butyl
<b>A-6</b>	Acetyltri-n-hexyl Citrate	ATHC	OAc	n-Hexyl
<b>B-6</b>	n-Butyryltri-n-hexyl Citrate	BTHC	OBu	n-Hexyl

Product Data	C-2	A-2	C-4	A-4	A-6	B-6
<b>CAS Number</b>	77-93-0	77-89-4	77-94-1	77-90-7	24817-92-3	82469-79-2
<b>Molecular Weight</b>	276.3	318.3	360.4	402.5	486	514
<b>Molecular Formula</b>	C <sub>12</sub> H <sub>20</sub> O <sub>7</sub>	C <sub>14</sub> H <sub>22</sub> O <sub>8</sub>	C <sub>18</sub> H <sub>32</sub> O <sub>7</sub>	C <sub>20</sub> H <sub>34</sub> O <sub>8</sub>	C <sub>26</sub> H <sub>46</sub> O <sub>8</sub>	C <sub>28</sub> H <sub>50</sub> O <sub>8</sub>

## Properties - Table 1

Physical Properties	C-2	A-2	C-4	A-4	A-6	B-6
Appearance	Clear Liq.	Clear Liq.	Clear Liq.	Clear Liq.	Clear Liq.	Clear Liq.
Odor	Essentially odorless	Essentially odorless	Essentially odorless	Essentially odorless	Essentially odorless	Essentially odorless
Pour Point, °C	-45	-43	-62	-59	-57	-55
Viscosity @ 25°C, cps	35	54	32	33	36	28
<sup>1</sup> Volatiles, %	1.6	1.3	0.2	0.2	1.4	1.3
*Vapor Pressure, mm Hg @ 20 °C	6.4 x 10 <sup>-3</sup>	5.7 x 10 <sup>-3</sup>	9.6 x 10 <sup>-2</sup>	5.2 x 10 <sup>-2</sup>		1 x 10 <sup>-9</sup>
Flash Point (COC), °C	155	188	185	204	240	204
Solubility @ 25°C, g/100ml in:						
Water	5.5	0.72	<0.1	<0.1	<0.1	<0.1
Acetone	∞	∞	∞	∞	∞	∞
Ethanol	∞	∞	∞	∞	∞	∞
Heptane	Insoluble	Insoluble	∞	∞	∞	∞
Isopropanol	∞	∞	∞	∞	∞	∞
Toluene	∞	∞	∞	∞	∞	∞

\*Citrates with vapor pressures less than 0.10 mm Hg @ 20 °C are exempt from VOC reporting to CARB under Section 94510(d)(1)

<sup>1</sup>Modified EPA Method 24: An accurately weighed 10 g sample in a 250 ml beaker is kept @ 110 °C for 1 hour, then reweighed. Reported as average weight loss from at least 4 trials.

Specifications	C-2	A-2	C-4	A-4	A-6	B-6
Ester content, %	99.0 min.	99.0 min.	99.0 min.	99.0 min.	99.0 min.	99.0 min.
Identification, IR	Meets test	Meets test	Meets test	Meets test	Meets test	Meets test
Neutralization # (mg KOH/g)	0.2 max.	0.2 max.	0.2 max.	0.2 max.	0.2 max.	0.2 max.
Color, APHA	50 max.	50 max.	50 max.	30 max.	100 max.	100 max.
Water, %	0.25 max	0.3 max	0.3 max	0.25 max	0.15 max	0.15 max
Heavy metals, ppm	10 max	10 max	10 max	10 max	5 max	5 max
Specific Gravity @ 25/25°C	1.135-1.139	1.135-1.139	1.037-1.045	1.045-1.055	1.003-1.007	0.991-0.995
Refractive Index @ 25°C/D	1.440-1.442	1.432-1.441	1.443-1.445	1.4410-1.4425	1.445-1.449	1.444-1.448

## Resin Compatibility

**Citroflex** plasticizers are compatible with a wide range of hydrophilic and lipophilic polymers and polymer blends. They are also compatible with several non-citrate plasticizers, allowing the formulator to obtain performance parameters not available with individual plasticizers. Epoxy soya oil (ESO), for example, is less expensive than the **Citroflexes**. When blended with **Citroflex A-4**, ESO reduces plasticizer cost while contributing a reduction in volatility and extraction characteristics. Performance data comparing various blends of **Citroflex A-4**/ESO with A-4 alone as plasticizers for medical grade PVC (PolyOne Geon 110X-500\*) is presented in Table 3.

**Citroflex A-4** is also a suitable replacement for di-2-ethylhexyl adipate (DEHA) for food contact applications, providing an alternate for DEHA where there has been some concern for the public health. Performance data reflecting replacement of DEHA with **Citroflex A-4** as co-plasticizers for the polymeric plasticizer Reoplex® 346 (Novartis)\* for medical grade PVC (PolyOne Geon 110X-500\*) is presented in Table 4.

A comparison of performance data for **Citroflex A-4**, **A-6**, and **B-6** versus DEHA and di-2-ethylhexyl phthalate (DEHP) as the sole plasticizers for medical grade PVC (PolyOne Geon 110X-500\*) is presented in Table 5.

\* Geon is a registered trademark of PolyOne  
Reoplex is a registered trademark of Novartis Ag

# Resin Compatibility

**Table 2**

Polymer	Citroflex Ester					
	C-2	A-2	C-4	A-4	A-6	B-6
Cellulose acetate (B)	C	C	P	P		
Cellulose acetate-butyrate	C	C	P	P		
Cellulose nitrate	C	C	C	C		
Chlorinated rubber	C	C	C	C	C	C
Ethyl cellulose	C	C	C	C		
Nitrocellulose	C	C	C	C		
Polyacrylate	C	C	C	C	C	
Polyacrylate/methacrylate	C	C	C	C		
Poly caprolactone (B)	C	C	C	C	C	C
Polyvinyl acetate	C	C	C	C		
Poly lactic acid (PLA) (B)	C	C	C	C		
Polyhydroxy butyrate/ valerate (PHB/V) (B)	C	C	C	C	C	
Polyvinyl chloride	C	C	C	C	C	C
Polyvinyl chloride-acetate	C	C	C	C		
Polyvinylidene chloride	C	C	C	C		
Polyvinyl butyral	C	C	C	C		
Polyvinyl pyrrolidone	C	C				
Polyurethane				C	C	C
Polyethylene terephthalate	C	P	P	I	I	I
Polyethoxy ether ketone	P					
Starch acetate (B)	C	C	P	P		

Legend: **C** = Compatible, **P** = Partially compatible, **I** = Incompatible,  = Unknown  
**(B)** denotes a biodegradable resin



# Performance Testing of Plasticizers

All performance tests were made with samples cut from 70 mil compression molded stock except for extraction tests, which were conducted on 40 mil samples. The plastic stock was blended and two-roll milled for 5-10 minutes at 325 to 340 degrees F. The milled stock was compression molded for 3 minutes at 340 to 360 degrees F and 32,000 psi to form the 40 and 70 mil sheets, then conditioned for 48 hours at 75 degrees F for evaluation. The performance data were obtained by accepted ASTM methods. Any modifications are included below:

## Comparative Plasticizer Performance Data

### Typical Test Formulation:

This formula demonstrates the performance of the **Citroflex** plasticizers in comparison with di-(2-ethylhexyl) phthalate (DEHP) and di-(2-ethylhexyl) adipate (DEHA). Medical grade PVC plastic stock was blended and two-roll milled for 5-10 minutes at 325 to 340 degrees F. The milled stock was compression molded for 3 minutes at 340 to 360 degrees F and 32,000 psi to form the 40 and 70 mil sheets, then conditioned for 48 hours at 75 degrees F for evaluation. The only change was in the nature of the selected plasticizer.

Item	Description	Parts by Wt
Resin	Geon 110X-500*	100.00
Plasticizer	(See Table 5)	50.00
Stabilizer	Calcium/Zinc	2.50
Lubricant	Stearic Acid	0.25

\*Geon is a registered trademark of PolyOne

**Table 3**

Characteristics	Plasticizer			
	DEHP	DEHA	A-4	B-6
Hardness	79	78	78	81
Tensile Strength, psi	2748	1797	2862	2924
Ultimate Elongation, %	395	414	400	427
100% Modulus, %	1368	1092	1348	1362
Brittle Point, °C	-24.5	-56.5	-18.5	-33.5
Volatile loss (air), %	4.8	7.1	12.1	1.7
Volatile loss (A/C), %	3.4	7.6	7.0	1.4
Water extraction, %	0.7	1.5	1.2	1.7
Soapy water extraction, %	2.7	11.0	9.5	2.2
ASTM Oil #3 extraction, %	11.4	34.7	10.9	15.7

## Specific Applications of the Citroflex Esters

### Triethyl Citrate (Citroflex 2)

**Citroflex 2** does not support fungal growth. The Food Grade (sold as TEC-FCC) has been accepted as a direct food additive by the US Food & Drug Administration. **Citroflex 2**, the commercial grade, is recommended as a plasticizer for cellulosic derivatives as well as natural resins such as dammar and ester gums. Due to its limited oil solubility, grease resistance of polymers formulated with **Citroflex 2** is enhanced. **Citroflex 2** also imparts improved light-fastness to lacquer formulations. In the personal care area, Citroflex 2 is used as a fixative for perfumes and as a plasticizer and film strengthening agent in hair sprays, nail polishes, and as an active in deodorants. The NF version of **Citroflex 2 (TEC-NF)** is widely used in pharmaceutical coatings.

### Acetyltrietyl Citrate (Citroflex A-2)

**Citroflex A-2** is recommended for use with cellulosic derivatives. It offers low warping characteristics with cellulose acetate. **Citroflex A-2** has been accepted for use as a plasticizer in food wrap films by the US Food & Drug Administration. **Citroflex A-2** is used as a fixative for perfumes and as a plasticizer and film strengthening agent in hair sprays, and nail polishes, as well as a component of various ink formulations. A special version for use in pharmaceutical coatings is sold as **ATEC, NF**.

### Tri-n-butyl Citrate (Citroflex 4)

**Citroflex 4** does not support fungal growth. It is an excellent plasticizer for both cellulosic derivatives and vinyl resins. It provides improved light stability when used in cellulose acetate. **Citroflex 4** is also an excellent defoaming agent in proteinaceous solutions. A special version for use in pharmaceutical coatings is sold as **TBC, NF**.

### Acetyltrietyl Citrate (Citroflex A-4)

**Citroflex A-4** is widely used in food contact polymers. It provides many improvements over dibutyl phthalate in cellulose nitrate films, including lower volatility, better resistance to yellowing, and better adhesion to metals. **Citroflex A-4** is effective in solution coating both paperboard and foil. It is an excellent plasticizer for vinyl toys.

**Citroflex A-4 Special** is developed and recommended for medical articles and similar sensitive applications. It is manufactured in a unique, patented process. A special version for use in pharmaceutical coatings is sold as **ATBC, NF**.

### Acetyltrietyl Citrate (Citroflex A-6) and n-Butyryltrietyl Citrate (Citroflex B-6)

**Citroflex A-6** and **B-6** are specially formulated citric acid esters for use in PVC medical articles such as tubing and IV bags where the content medium is aqueous-based. **Citroflex B-6** has low extractability into lipid media, making it particularly useful for blood products. It nearly duplicates the properties of di-(2-ethylhexyl) phthalate.

**Table 4**

Application	Recommended Citroflex Ester					
	C-2	A-2	C-4	A-4	A-6	B-6
<b>Medical Plastics</b>						
Topical bandages	X	X	X			
Patch delivery systems	X	X				
Aqueous pharmaceutical coatings	TEC-NF	ATEC, NF	TBC, NF	ATBC, NF		
Extra-corporeal tubing				X	X	X
Blood bags					X*	X*
Cellulosic molding resins	X	X				
I.V. solution containers and sets					X	X
Catheters					X	X
<b>Food Contact Products</b>						
Food wraps and films (PVC & PVdC)				X		
Beverage tubing				X		
Crown liners				X		
Food containers				X		
Tinplate lubricant				X		
Aluminum foil coatings			X	X		
Dish detergent	X					
<b>Food Additives</b>						
Whipping agent in dried egg whites	TEC, FCC					
GRAS uses	TEC, FCC					
<b>Personal Care Products</b>						
Fixative/Carrier for perfumes	X	X				
Aerosol hair spray plasticizer	X	X	X			
Deodorant active	X					
Solvent/plasticizer for Nail polish/remover	X	X				
<b>Cellulosics</b>						
Cigarette filters	X					
Molded articles	X	X				
Films	X	X	X			
Coatings	X	X	X			
Nitrocellulose-based explosives/propellants		X		X		
<b>Other Industrial Uses</b>						
Children's toys				X		
Animal ear tags				X		
Ink formulations	X	X		X		
Defoaming agent		X				
Adhesives			X	X		
Pesticide Inerts	X			X		

• See patent notice on page 11

## Regulatory / Approval Status of Citroflex Esters

- **Vertellus Specialties Inc.** has submitted Drug Master Files for Citroflex 2 (TEC), Citroflex A-2 (ATEC), Citroflex 4 (TBC), Citroflex A-4 (ATBC), Citroflex A-6 (ATHC), and Citroflex B-6 (BTHC). A Device Master File has been submitted for Citroflex A-4 (ATBC).

- Citroflex A-6 and B-6 are intended for use as plasticizers for medical plastics.

- **USP/NF** A Monograph is listed for Triethyl Citrate (TEC)

Monographs are pending for ATEC, TBC, ATBC.

- Multiple Title 21, Code of Federal Regulations (CFR) listings for citrates confirm their acceptance for food and food contact products. (*See Table 5*)

- All have Kosher Certification per the Union of Orthodox Jewish Congregations of America

**Table 5**

Product	CFR Listing	Subject
Triethyl Citrate (TEC)	175.300	Resinous and polymeric coatings
(Citroflex 2)	175.320	Resinous and polymeric coatings for polyolefin films
	175.380	Xylene-formaldehyde resins condensed with 4,4' - isopropylidenediphenol-epichlorohydrin epoxy resins
	175.390	Zinc-silicon dioxide matrix coatings
	176.170	Components of paper and paperboard in contact with aqueous and fatty foods
	177.1210	Closures with sealing gaskets for food containers
	181.27	Prior sanctioned plasticizers
	182.1911	Generally recognized as safe as food additive in dried egg whites up to 0.25%
	184.1911	Generally recognized as safe and meets Food Chemicals Codex specifications
		Food Chemicals Codex Listing (FCC Grade)
		Flavor Extracts Manufacturers Association (FEMA) #3083
		EEC Directive 90/128 for Food Films, List 1 (Included on Positives List)
		EPA list of Inert Pesticide Ingredients
Acetyltriethyl Citrate (ATEC)	175.105	Components of adhesives
(Citroflex A-2)	175.300	Resinous and polymeric coatings
	175.320	Resinous and polymeric coatings for polyolefin films
	175.380	Xylene-formaldehyde resins condensed with 4,4' - isopropylidenediphenol-epichlorohydrin epoxy resins
	176.170	Components of paper and paperboard in contact with aqueous and fatty foods
	177.1210	Closures with sealing gaskets for food containers
	178.3910	Surface lubricants used in the manufacture of metallic articles
	181.27	Prior sanctioned plasticizers
		EEC Directive 90/128 for food films, List 8
Tri-n-butyl Citrate (TBC)	175.105	Components of Adhesives
(Citroflex 4)		EEC Directive 90/128 for food films, List 6B

Table 5 continues on page 12.

**Table 5** (continued from page 11)

Product	CFR Listing	Subject
Acetyltri-n-butyl Citrate (ATBC)	172.515	Synthetic flavoring substances and adjuvants
(Citroflex A-4 & A-4 Special)	175.105	Components of adhesives
	175.300	Resinous and polymeric coatings
	175.320	Resinous and polymeric coatings for polyolefin films
	175.380	Xylene-formaldehyde resins condensed with 4,4' - isopropylidenediphenol-epichlorohydrin epoxy resins
	176.170	Components of paper and paperboard in contact with aqueous and fatty foods
	177.1210	Closures with sealing gaskets for food containers
	178.3910	Surface lubricants used in the manufacture of metallic articles
	181.27	Prior sanctioned plasticizers
		Flavor Extracts Manufacturers Association (FEMA) #3080
		EEC Directive 90/128 for food films, List 8 (Dossier submitted for inclusion on Positives List)
		EPA list of Inert Pesticide Ingredients

## Literature and Samples

Additional information on the **Citroflex** esters can be found in the monographs offered as Technical bulletins 102-1, 102-2, 102-3, 102-4 and 102-5, 103 and 104. These bulletins as well as samples of all **Citroflex** products may be obtained by writing **Vertellus Specialties Inc.**, calling **Customer Service +1 (336) 292-1781** or at any **Vertellus Specialties Inc.** sales office or online at **www.vertellus.com**.

**Samples** are available in 16 ounce bottles.

### Packaging

**Citroflex** esters are available in tankcars, tank trucks, nonreturnable 55-gallon drums and nonreturnable polyethylene 5-gallon pails.

### References

Available upon request

### Patent Notice

**Vertellus Specialties Inc.** is the owner of patents relating to certain citrates and the use thereof. The sale of these citrates by Vertellus does not confer upon the purchaser any patent license, expressed or implied, to use the esters in blood products or for any other particular purpose. For additional information, please contact our sales department.

CITROFLEX is a registered trademark of Vertellus Specialties Inc..

**The information contained herein is true and accurate to the best of our knowledge. No warranty or guarantee is expressed or implied regarding the accuracy of such data. It is the user's responsibility to determine the suitability for his own use of the products described herein. Nothing herein shall constitute permission, inducement, or recommendation to practice any invention covered by any patent owned by Vertellus Specialties Inc. or by others, nor as a recommendation to use any product or to practice any process in violation of any law or government regulation.**

## Global Footprint



### Global Sales Offices, Manufacturing Facilities & Distributor Network

**Vertellus is a leading provider in the world of specialty chemicals for agriculture, nutrition, pharmaceutical, medical, personal care, plastics, coatings and industrial markets.**

- 500+ products, notably the world's first producer of pyridine
- 150+ years of experience in the development of specialty chemicals
  - 13 manufacturing plants on three continents

Besides being a global leader in the manufacture of picoline and pyridine products, we are also a leading producer of cyanopyridine, and nicotinic acid/amide.

We're recognized as the leading innovator in natural-based castor oil chemistry and citrate esters, providing performance solutions for a wide range of demanding applications for an ever-changing marketplace.

From crop protective chemicals to the highest standards of production for FDA-approved pharmaceutical applications, Vertellus consistently meets the challenge.



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