



VenPure® Polisher

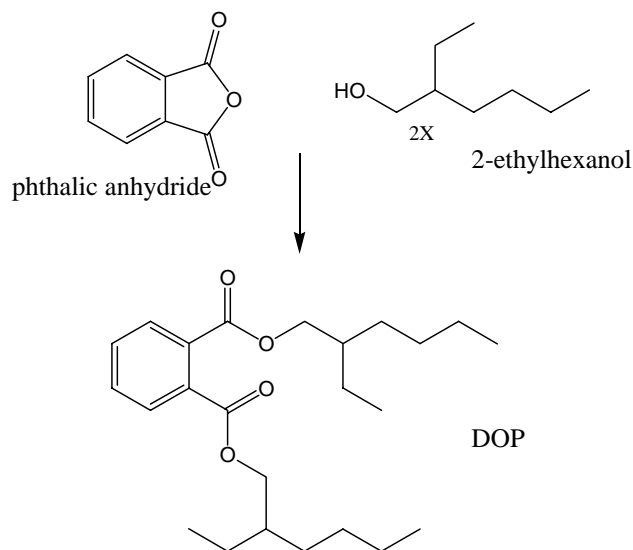
Improving the Color of Plasticizer Esters

Summary

The VenPure technology offers **a means of preventing discoloration** of plasticizer esters, either by pre-treatment of the alcohol stream or by post-treatment of the ester. VenPure treatment may allow the use of recycle alcohol streams while still obtaining acceptable ester grades.

The formation of colored bodies

One important plasticizer ester is DOP, Di-*sec*-OctylPhthalate. It is produced by esterification of phthalic anhydride with 2-ethylhexanol.



Plasticizer esters may suffer from discoloration, which causes the plasticizer to be sold as off-grade quality, or to be reworked to bring color within acceptable limits. Discoloration can be caused by :

1. the reaction conditions during esterification :
 - a. acid
 - b. high temperature
 - c. the presence of air
2. the quality of the starting materials
 - a. carbonyls
 - b. peroxides
 - c. metal contaminants

In particular, 2-ethylhexanol, which is produced via hydrogenation of 2-ethylhexenal, often contains unreduced species that will form colored bodies impurities upon the subsequent esterification reaction conditions. This is effect is even more pronounced for recycled alcohol streams.

VenPure benefits

- VenPure will *scavenge* the following *impurities* :
 - o peroxides
 - o carbonyl species
 - o metal contaminants impurities
- VenPure pre-treatment of alcohol or recycle alcohol will *inhibit color formation* during esterification
- VenPure post-treatment allows to *recover off-grade product* streams
- VenPure *dosage rates* are typically *low* – addition can happen with readily available dosage equipment
- Depending on the specifics of the esterification chemistry and equipment, VenPure Polisher products of different *physical forms* can be used:
 - o An aqueous solution
 - o Granules
 - o Caplets : for usage in a caplet bed

A typical VenPure Polisher treatment

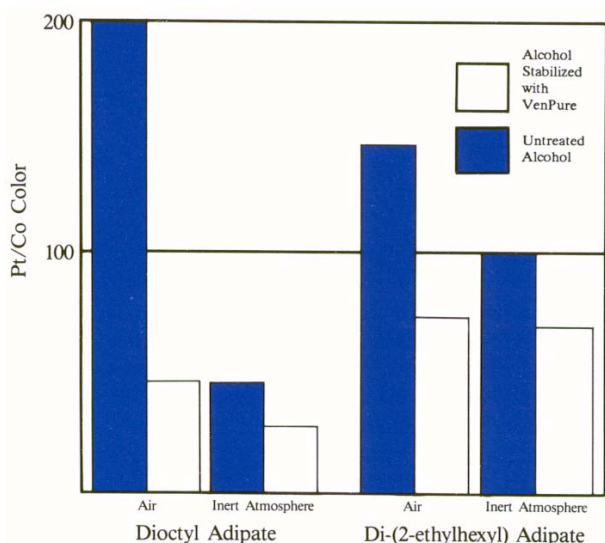
VenPure treatments are available for both alcohol pre-treatment, treatment of recycle alcohol, and ester post-treatment (see case studies). A typical alcohol pre-treatment consists of mixing the VenPure product of choice in the alcohol product stream, and allowing reaction for 1 hour at 50 – 80°C. This can happen during heating of the reactor, prior to the esterification reaction.

Depending on the specifics of the VenPure treatment, it may be necessary to adjust the pH prior to addition of the acid/anhydride product stream and/or prior to addition of the esterification catalyst. VenPure by-products products should not interfere with the esterification chemistry. In the rare case that they do, then a water wash of the alcohol product stream will be necessary.

Case Study 1 – pretreatment of alcohol

Commercial plasticizer alcohols are usually of high quality. Still, the addition of low levels (0.005-0.01%) of VenPure products results in significantly less color in the final ester products. This effect is especially enhanced if the esterification reaction does not occur under inert atmosphere.

Treatment in our lab has proven that pretreatment of 2-ethylhexanol and octanol results in esters which are significantly more stable towards oxidative color degradation. The alcohol is pre-treated with addition of 0.01% VenPure Polisher P, several hours prior to making the ester. Comparison of the esters produced in an inert atmosphere and air illustrate the extra protection against oxidative color formation provided by VenPure treatment.



Case Study 2 – pretreatment of recycled alcohol

Recycled alcohols typically contain a high concentration of contaminants. Lab studies have proven that the discoloration of plasticizer esters can be significantly decreased if recycle alcohol streams are pre-treated with VenPure. The examples hereunder were using between 0.05 and 0.1% VenPure Polisher P.

Recycle alcohol	Anhydride/Acid	Color with no treatment	Color with VenPure treatment
Isononanol	Phthalic	12 gardner	6 gardner
Octanol	Adipic	2 gardner	1 gardner

In another study, on a recycle 2-ethylhexanol containing 25% water, the total carbonyl content decreased from 2300 to 480 ppm upon addition of 1.2% VenPure Polisher S (an aqueous solution). Treatment was at 80°C for about 1 hour. The majority of contaminants were found in the water phase. A similar decrease of carbonyls was found for water-free recycle ethylhexanol.

Recycle alcohol	VenPure Polisher S	Reaction T°C	Carbonyls before treatment (ppm)	Carbonyls after treatment (ppm)
Ethylhexanol/water	0.83%	80	2300	480
Ethylhexanol	0.57%	65	6000	1600

Alternatively, a solid form of VenPure Polisher can be added to recycle alcohol streams. One study has proven to bring the aldehyde content from 31 mg/kg to 11mg/kg upon addition of 0.05% VenPure Polisher P. Reaction was allowed for 1hour at 55°C.

The optimum treatment for recycle alcohols is to have them circulating over a Packed Bed of VenPure caplets at temperatures between 50 and 80°C. By allowing sufficient circulation time, the amount of oxidized impurities can be reduced to non-detectable. A Packed Bed allows improved purification kinetics by means of improved mass transfer and surface interaction.

Case Study 3 : post-treatment of esters

In addition to preventing ester color development, VenPure treatment may also effectively reduce colored species after they have formed. Color improvement is typically achieved by mixing 0.1 – 0.4% of VenPure Polisher S with the ester and filtering through diatomaceous earth.

Sample	Pt/Co Color	
	Untreated	After VenPure Treatment
Phthalate Ester	60	20
Phthalate Ester	200	60
Phthalate Ester	250	150
Phthalate Ester	30	20
Trimellitate Ester	350	90
Trimellitate Ester	150	110

Toxicity and First Aid

1. VenPure Polisher S has dermal LD₅₀ of 100-500 mg/kg and, like 50% caustic soda, (NaOH) solutions can cause skin burns and irritations. The acute oral LD₅₀ of VenPure Polisher is 500-1000 mg/kg.
2. VenPure Polisher S is *very corrosive to the eye* and should be handled according to generally accepted procedures for corrosive chemicals. In case of accidental contact, flush eyes with water and *seek immediate medical attention*.
3. Precautions should be taken to avoid direct skin contact or ingestion. In case of accidental contact, flood the affected area with copious amounts of water and then wash skin with soap and water.

Product Handling

1. *Personal Protection:* Protective rubber gloves, clothing, face shield or safety (splash) goggles should always be worn when handling VenPure Polisher .
2. *Handling:* In general, VenPure PolisherS should be handled in the same manner as 50% caustic soda. It is classified as a non-flammable, corrosive liquid, and it is stable to shock. Due to the presence of NaOH, VenPure Polisher absorbs CO₂ forming insoluble carbonates. Consequently, it should not be unnecessarily exposed to air for extended periods.

VenPure Polisher S will decompose and evolve hydrogen if overheated, subjected to neutral or acidic pH conditions, or brought into contact with oxidizing agents, metal salts or fine metallic precipitates of Ni, Co, Cu or Fe. VenPure reactions should always be carried out in adequately vented vessels with standard provisions for pressure relief. A nitrogen atmosphere is also recommended, as well as explosion proof equipment with proper grounding.

3. *Storage:* Accepted storage procedures for VenPure Polisher S are the same as those for 50% liquid caustic soda.

Under normal storage conditions, the decomposition of VenPure Polisher S is less than 0.01% per year. During extended storage under adverse conditions, H₂ pressure may develop over the solution. All closed containers should have at least 10% free volume and be checked periodically. Under these conditions, pressure build-up will be less than 1 psi per year at normal storage temperatures.

Storage

VenPure Polisher S can be stored in stainless steel, mild steel, or approved fiberglass vessels. Stainless steel (316 SS or 304 SS) is recommended for piping, valves, pumps, etc. VenPure Polisher must NOT be stored in vessels which react with caustic soda, such as aluminum. Storage tanks should be adequately vented to minimize hydrogen gas build-up.

VenPure Polisher S should be stored at *temperatures* above 65° F (18° C) to improve handling. The solution becomes viscous below 60° F (16° C) and can crystallize at temperatures below 55° F (13° C). To liquify, warm slowly to 70-90° F (21-32° C), making sure the container is vented; do not use live steam. The warmed material should then be agitated by rolling the container, or recirculated with a high volume pump until a homogeneous solution is obtained.

If piping used to transfer VenPure Polisher S is exposed to temperatures below 55°F (13°C), it should be heat traced to improve handling. However, precautions should be taken to avoid excessively high temperature since VenPure Polisher may decompose resulting in the evolution of hydrogen gas and possible excessive line pressure.

Shipping and Waste Disposal

VenPure Polisher has been classed as a 'corrosive liquid' under US DOT regulations.

1. VenPure Polisher S is a corrosive material (EPA hazardous waste #D002) and must be disposed of accordingly. VenPure Polisher can be disposed of (hydrolyzed) by initial dilution with a large excess of water, followed by slow addition of a dilute solution of acetic acid or acetone to the mixture. This procedure should be performed in a well ventilated area.

Provisions should be made to safely vent hydrogen gas given off during neutralization. VenPure Polisher should not be flushed to the sewer.

2. In case of accidental spillage, absorb the VenPure Polisher with an inert material such as sand or dolomite. Absorbed material should be hydrolyzed as described above.
3. Any vessels which have been used for reactions or storage of VenPure Polisher should be carefully vented, drained, washed, and adequately flushed with nitrogen and air before any repair operations are undertaken. Exposure to an open flame (e.g., welding torch) should be avoided.

Please feel free to contact us via ... Hvenpure@rohmbaas.com

Updated information can be found at : [Hhttp://www.venpure.com/H](http://www.venpure.com/H)

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