



"Purification of Higher Alcohols Via Packed Bed and Charge Pot Additions of VenPure® Polisher Products"

Summary

VenPure products effectively reduce trace levels of carbonyls, organic peroxides and metal impurities in higher alcohols and amines. The presence of these impurities can result in color and odor problems for a manufacturer or end user.

VenPure Polisher C is a caplet that allows usage in a packed bed or a charge pot, providing large surface contact with the process and enhanced reducing efficiency. The packed bed design makes it possible to control the polishing efficiency, yielding carbonyl reductions of 90% or more and color reductions of 50% or more at cost effective treatment levels. Successful purifications have been conducted on C₈ through C₁₈ alcohols.

Technology Description

In the manufacture of surfactants and detergents, the presence of impurities in raw materials can result in color, odor, U.V. absorbance and product stability problems. These problems are the result of trace levels of oxidized impurities such as carbonyls, organic peroxides, and metal ions.

Traditional means of removing trace impurities are adsorption, distillation, hydrogenation, or oxidation. These traditional purification methods, if they can be used, are usually very costly. They often require large capital investments and have high energy requirements.

An alternative purification method exists with the use of packed beds of VenPure Polisher C. These beds can be easily incorporated into an existing plant process on a batch or continuous basis with a minimal capital investment.

The use of VenPure Polisher C packed beds expanded in recent years due to the associated efficiency and convenience of operation. Packed beds provide good mixing and a large surface area. Since the chemistry occurs in solution, the apparent limiting factor to the reaction kinetics is the rate of dissolution and solubility of a polishing agent. The bed characteristics enhance the rate of dissolution and help to increase the overall kinetics of these treatments.

VenPure Polisher C – Product Properties

Form:	White crystalline solid
Density @ 25°C:	0.54 g/mL
Void Space :	+/- 48%
Weight :	+/- 1.0 g per caplet
Melting point:	Decomposes above 400°C without melting



Rohm and Haas Company's VenPure products are available in forms other than caplets. One class of formulations that is used for the industrial purification of Fatty Alcohols, are aqueous solutions.

VenPure Benefits

- **Removal** of oxidized impurities, such as **carbonyls**, organic peroxides and metal ions
- **Decolorization** of the fatty alcohol product stream
- **Inhibit discoloration** upon subsequent reactions such as ethoxylation

VenPure treatment typically results in 80 – 90% reduction of initial carbonyl concentrations. At reaction temperatures between 40 °C and 110 °C, contact times are usually less than 10 minutes. Depending on the set up of the bed, this will require multiple treatment cycles.

Typically, reducing a Total Carbonyl Concentration of 100 mg/kg as CO requires less than 100 mg/kg VenPure Polisher C, using a packed bed.

One possible set-up, is to use a small bed for dissolution of the *full* caplets' bed volume into the fatty alcohol product stream by recirculating.

Similar packed bed polishing treatments can be set up for decolorization and/or color stabilization of amines and alkanolamines.

Experimental:

The experimental set-up for packed bed equipment models a batch recycle reactor of tubular flow type. The objective of a packed bed laboratory evaluation is to determine the contact time necessary to achieve the desired reduction in carbonyl level, typically 90%. Optimum contact time is determined by periodically analyzing samples for boron and carbonyl and plotting the results. Once the optimum contact time has been derived, a packed bed can be sized for commercial operation.

Results and Discussion:

In one laboratory study, C₈-C₁₀ alcohol samples were treated in a packed bed at 40°C. Carbonyl levels (measured as C=O, MW=28) were reduced by 90% after 1 minute of contact time. Treatments were accomplished with 180 ppm to 270 ppm VenPure Polisher C.

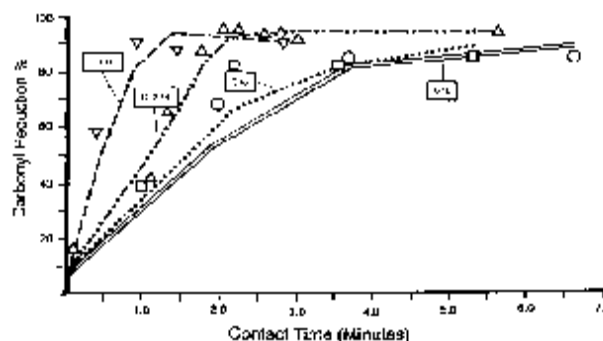
In other studies, C₁₂-C₁₄ alcohols were treated at 80°C, with carbonyl levels generally reduced by 90% within 2 minutes of contact time. Even higher carbon chain length alcohols (C₁₆ and C₁₈) were treated at 110°C, with carbonyl reductions of 85% in 2 minutes and 4 minutes of contact time, respectively.

Table I
Packed Bed Purification of C₈-C₁₈ Alcohols

Alcohol Description	Treatment Temp.	Contact Time	C=O Reduction
C ₈ -C ₁₀	40°C	0.9 min.	90%
C ₁₀	40°C	6 min.	90%
C ₁₂ -C ₁₄	80°C	2 min.	90%
C ₁₆	110°C	2 min.	85%
C ₁₈	110°C	4 min.	85%

The critical factors in accomplishing the desired polishing are the solubility and the rate of dissolution of VenPure Polisher C. The solubility of the VenPure Polisher C in an alcohol process stream is affected by the carbon chain length of the alcohol, the amount of lower alcohols and water present, and the treatment temperature. The rate of dissolution is enhanced through better mass transfer at the solid/liquid interface. Immobilizing the reagent in a packed bed/charge pot facilitates increases surface contact and hence better mass transfer. Laboratory experiments have shown that a particular treatment which required 24 hours of stirring in a flask to obtain 50% C=O reduction, can be achieved in a pellet bed with 2 minutes of contact time yielding 90% C=O reduction.

Figure I
Carbonyl Reduction vs. Contact Time for C₈ Through C₁₈ Alcohols



Packed Bed Calculations:

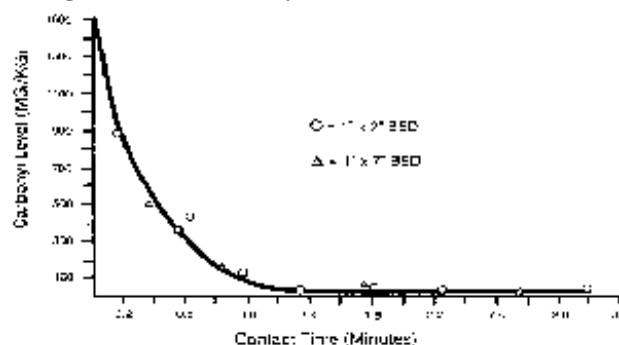
The contact time is the average time any unit volume of a process stream is in contact with the VenPure Polisher.

The Contact Time per cycle is determined as $\theta = V/F$

- F = Flow rate through the bed
- V = Void space in packed section = $V_t - V_c$
 - V_t = Total volume of packed section in column
 - V_c = Volume occupied by VenPure Polisher C

The utility of this calculation is shown in Figure II, which compares data for a C₁₂-C₁₄ alcohol treated on a 1-inch diameter by 7 inch deep packed laboratory column to that of a 1 inch diameter by 2 inch deep packed laboratory column. This shows that contact time is independent of bed geometry provided reasonable mass transfer is obtained.

Fig. II : Bed Geometry: CO versus Contact Time



Pilot Plant Studies:

In-house studies on a larger scale are possible with Rohm and Haas' skid mounted pilot plant system (5ft long, 8inch diameter). This unit works on the same principle as the smaller lab-scale system. However, the pilot scale system allows treatments to be studied on a larger scale with better fluid flow conditions. This unit is available for on site evaluations.

Toxicity and First Aid

1. VenPure Polisher C has an acute dermal LD₅₀ on dry skin of 4-8 g/kg, and is not a skin sensitizer. However, severe irritation and skin burns may result when VenPure products come into contact with moist skin. The acute oral LD₅₀ of VenPure Polisher C is 50-100 mg/kg. The reaction or decomposition product of VenPure products is considered slightly toxic orally (LD₅₀, 2000-4000 mg/kg), and non-toxic dermally.
2. All precautions should be taken against ingestion of VenPure products, inhalation of the dust, or contact with skin. In case of accidental contact with skin, the particles should be brushed off and the affected areas flooded with water. VenPure products and concentrated solutions of these are *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.*

Waste Disposal

1. VenPure products and their solutions containing can be disposed of (hydrolyzed) by dissolving in a large excess of water, followed by slow addition of a dilute solution of acetic acid or acetone in a well ventilated area. Provisions should be made to safely vent hydrogen gas given off during the decomposition of unreacted VenPure products and their solutions. VenPure products and their solutions should not be flushed to the sewer.
2. In case of accidental spillage, absorb the VenPure product with an inert material such as sand or dolomite. Absorbed material should be allowed to weather in an outdoor disposal area or hydrolyzed as per above.
3. Any vessels which have been used for storage or reactions of VenPure products should be carefully vented, drained, and adequately flushed with water and purged with nitrogen or air before any repair operations are undertaken. Exposure to an open flame (e.g., welding torch) should be avoided. Feel free to contact Rohm and Haas for more detailed procedures.

Product Handling and Storage

1. Personal Protection:
Protective rubber gloves, clothing and safety goggles should always be worn when handling VenPure products and their solutions. Dust respirators may be worn when handling VenPure Polisher C.
2. Handling:
VenPure Polisher C is classified as *Division 4.3 Dangerous When Wet* materials. It is stable to shock and does not ignite on contact with moisture, but forms a dihydrate which slowly hydrolyzes. VenPure Polisher C is hygroscopic and should not be unnecessarily exposed to air or moisture. It is stable indefinitely in dry air or in sealed containers. VenPure products may decompose and evolve hydrogen if overheated, subjected to neutral or acidic pH, or brought into contact with oxidizers, metal salts or finely divided metallic precipitates of nickel, cobalt, copper, or iron. Reactions of VenPure Polisher C should always be carried out in adequately vented vessels with standard provisions for pressure relief. A nitrogen atmosphere is also recommended. Rohm and Haas recommends to use explosion proof equipment with proper grounding.
3. Storage:
VenPure products should be stored in closed containers in a dry, cool and well ventilated area and kept separate from acids and oxidizing materials. Partially consumed containers should be carefully resealed. Solutions of VenPure products may be stored in stainless steel, mild steel, PE, PP, or approved fiberglass vessels that are adequately vented to the outside atmosphere. Caustic solutions of VenPure products should not be stored in vessels which react with NaOH, such as aluminum. Also, because of the risk of hydrogen evolution associated with improper storage, glass containers should *never* be used to store any VenPure products.
4. Firefighting:
VenPure Polisher C will ignite in air from a free flame due to hydrogen formed from thermal decomposition, continuing to burn as H₂ is evolved. It may ignite when brought in contact with acids, oxidizers, or transition metal salts or precipitates. The non-volatile product of combustion is NaBO₂. Fire extinguishers available where VenPure Polisher C is stored or used, should only be of the dry chemical type. ***WATER, CO₂ OR HALOCARBON extinguishers MUST NOT BE USED.***

Please feel free to contact us via ...

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Updated information can be found at :

<http://www.venpure.com/>

Find your local Rohm and Haas Representative :

<http://www.venpure.com/contact.html>