TOX-006
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Toxicology / Regulatory / Health, Safety & Environmental Studies of Powdered Carbopol® Polymers

Effect of Microbial Activity

Powdered Carbopol® polymers do not support bacterial or fungal growth. These Carbopol polymers do not, however, prevent the growth of bacteria or fungus associated with nutrients found in normal water systems.

Biotreatability of Carbopol Polymers

The environmental fate of chemicals is increasingly becoming a concern of consumers and responsible chemical producers and formulators. For chemicals found in products that are disposed "down the drain", it is important they do not pass through the municipal waste treatment facility into lakes and rivers. To prevent this, such chemicals may either be biodegraded or removed during the normal waste-water treatment.

This section is designed to answer three questions about powdered Carbopol polymers:

1. Are these polymers biodegradable?
2. Do they inhibit or harm the bacteria found in treatment facilities?
3. Are they removed during normal wastewater treatment?

Biodegradability of Carbopol Polymers

Biological oxygen demand tests were performed on a number of Carbopol crosslinked polyacrylic acid polymers (Dr. Brian Arbuckle, University of Akron, April 16, 1992). In each case, the results were the same: the biological oxygen demand (BOD) was zero. In essence, the same characteristics which give these polymers excellent shelf life in severe environments also prevent them from degrading in a wastewater treatment facility.

Inhibition of Bacteria by Carbopol Polymers

During the above BOD testing, the effect of powdered Carbopol polymers on bacteria was examined. In the concentrations tested (0.85, 1.7, 8.5, 17 and 42 mg/L), this work found none of the polymers to be inhibitory to the bacteria typically found in a wastewater treatment facility. Thus, while these polymers are not degraded, they neither harm the bacteria nor render it less effective.

Removal of Carbopol in a Treatment Facility

If powdered Carbopol polymers are not degraded in a typical wastewater treatment facility, they must be removed in some fashion or else they would pass through to the environment. Tests were performed (Dr. Brian Arbuckle, University of Akron, April 16, 1992) to determine if the polymers would be removed during typical wastewater treatment by sorption onto the biomass. (When the term sorption is used, it usually means either a physical adsorption or absorption on the solid. It is also possible that material could be trapped in the biological floc and therefore be removed by that mechanism. Sorption will be used here to indicate removal, not necessarily the mechanism.)

The tests were performed at significantly higher concentrations of polymer than would be expected in real life (two to three orders of magnitude greater).

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This was done so the polymer could be detected analytically, but also results in a more severe test than would be expected in an actual municipal wastewater treatment situation. A standard U.S. EPA Synthetic Waste Recipe[1] was used and mixing times representative of typical municipal treatment facilities were employed.

The above tests show that – within experimental test sensitivity – Carbopol polymers are completely sorbed or trapped onto the biomass at polymer concentrations up to 16 ppm. Thus, instead of passing through to lakes and streams, these polymers are removed with the biomass and disposed or incinerated.

Conclusions

Based on the above testing, it can be said that powdered Carbopol polymers:

1. are not biodegradable,
2. do not inhibit waste treatment bacteria, and
3. do not pass through typical wastewater treatment to the environment, but are instead removed with the biomass.

Effect on Aquatic Life

The effect of powdered Carbopol polymers on aquatic life (Bluegill, Sunfish and Daphnia Magna) was tested using a 96-hour static acute toxicity test. Results show that Carbopol polymers exhibit a low degree of aquatic toxicity. The death of fish is believed to be caused by exhaustion (due to the high viscosity of the solution) rather than oxygen starvation.

An additional study was undertaken to evaluate the aquatic toxicity of powdered Carbopol polymers. The data indicated that Carbopol polymers have no effect on mysid shrimp (Mysidopsis bahia) at a 100% saturation concentration.

The objective of the study was to determine the 96-hour LC50 and 96-hour NOEC (No Observed Effect Concentration) of the Carbopol polymer for mysid shrimp under static-renewal test conditions. Based on the saturation concentration of the test substance in dilution water, the Carbopol polymer 96-hour LC50 and 96-hour NOEC for mysid shrimp are both greater than 100% saturation concentration.

[1] Barth, E.F., et al., "Biodegradation Studies of Carboxy-methyl Tartonate," In-house U.S. EPA report, (1978), U.S. EPA contact: Henry Tabak.

Eye Irritation

Dispersions (pH 3 and below) of powdered Carbopol polymer are eye irritants. Experience has shown that the dry powder inadvertently dusted into the eyes of workers caused only minor irritation when it was promptly removed by flushing the eyes with a 1% physiological saline solution. Water swells Carbopol polymer into a gelatinous film, which may be difficult to remove from the eye; therefore, the possibility of eye damage may be greater than if a saline flush is used.

Use of a 1% physiological saline solution is the treatment of choice. However, in the event that one is not available, the eye should be flushed with water.

Toxicology of Carbopol Polymers

Powdered Carbopol polymers have a long history of safe use in cosmetic and pharmaceutical products. They have been used globally in cosmetic and topical pharmaceutical applications for forty years. The more recently commercialized Carbopol polymers are polymerized in a cosolvent system of ethyl acetate and cyclohexane. The cosolvents ethyl acetate and cyclohexane display extremely low order of both acute and chronic toxicities. Ethylacetate is approved as a "generally recognized as safe" (GRAS) direct food additive and cyclohexane is approved as an indirect food additive.

Toxicological studies have been conducted on each of the families of products discussed in this bulletin. Following are the results of each study.

Toxicology of Carbopol Polymers as a Class

The powdered Carbopol polymers, like other high molecular weight polymers, demonstrate a low toxic and irritation potential based on their physical and chemical properties. Accordingly, such cross-linked, high molecular weight acrylic polymers have been found safe for use in a wide variety of cosmetics, detergents and pharma-ceuticals by appropriate regulatory and non-regulatory bodies concerned with such products.

The chemical composition and the chemical and physical properties of the powdered Carbopol polymers suggest that similar toxicological properties are to be expected with these polymers. Powdered Carbopol polymers are crosslinked homopolymers of acrylic acid or crosslinked copolymers of acrylic acid with a minor acrylic comonomer.

The molecular weight range of these polymers is estimated to be from 740,000 to several billion. There are no methods available to measure the actual molecular weight of a crosslinked (i.e. 3-dimensional) polymer of this type. As discussed in Section 1.2, the backbone of the homopolymer Carbopol is the same. The main difference is related to crosslinked density and molecular weight, rather than the crosslinker used.

The three-dimensional nature of these polymers confers some unique characteristics, such as biological inertness, not found in similar linear polymers. The Carbopol polymers are hydrophilic substances that are not soluble in water. Rather, these so-called "water soluble" polymers swell when dispersed in water forming a colloidal, mucilage-like dispersion.

Many of the Carbopol polymers have found diverse applications in the cosmetic, detergent and pharmaceutical industries. Due to their physical properties, inertness and low toxicity, Carbopol polymers have been used in such preparations as suspending, flow control, thickening and emulsion stabilizing agents.

Carbomer is the generic (i.e. non-proprietary) name adopted by USP-NF, United States Adopted Names Council (USAN) and CTFA for various Carbopol homopolymers. The Cosmetic Ingredient Review (CIR) Expert Panel in their assessment* of the safety of the carbomers for cosmetic ingredients summarized the toxicity of the carbomers as follows:

Acute oral studies with rats, guinea pigs, mice, and dogs showed that carbomers have low toxicities when ingested. No mortalities occurred in rabbits injected intravenously with 1%, 2% or 3% carbomer in aqueous solution at a dose of 5 mL/kg. Rabbits showed minimal skin irritation when tested with 100% carbomer, and zero to moderate eye irritation when tested with carbomers and/or their various salts at concentration of 0.20-100%.

Subchronic feedings of rats with doses up to 5.0 g/kg/day carbomer (49 days) and of rats and dogs with up to 5.0% carbomer in the diet (21 and/or 90 days) resulted in lower than normal body weights. In rats fed carbomer at dietary levels of 5.0% for 90 days, absolute liver weights and liver to body and brain weight ratios were reduced, but no pathological changes were observed.

When dogs were chronically fed up to 1.0 g/kg/day carbomer (32 months), and when rats chronically received less than 4.0% carbomer in their diet (six and one-half months), there was no significant effect on body weight, food consumption, mortality, behavior or blood chemistries. Hematology, gross pathology, histology, and urinalyses of treated animals were comparable to those of controls. Rats fed carbomer at dietary levels of 0.1%, 0.5% or 5.0% for six and one-half months exhibited various organ weight changes. Dogs fed 0.5 or 1.0 g/kg/day carbomer for six and one-half months manifested gastrointestinal irritation and marked pigment deposition within Kupffer cells of the liver.

Clinical studies with carbomer and its various salts showed that these polymers have low potential for skin irritation and sensitization at concentrations of 0.5%, 5.0%, 10.0% and 100%. When tested on humans at 1.0% concentration, carbomer and the various salts also demonstrated low potential for skin irritation and sensitization. Further, formulations containing up to 0.25% carbomer demonstrated low potential for human skin irritation, sensitization, phototoxicity, and photo-contact allergenicity.

Clinical data for assessing the skin irritation and sensitization potential of carbomer were limited to studies in which concentrations of only 1.0% were tested. Clinical data for assessing phototoxicity* and photo-contact allergenicity were limited to formulation studies in which concentrations of only 0.25% carbomer were tested.

The CIR Expert Panel called attention to the presence of benzene as an impurity in certain carbomers and recommended that efforts be made to reduce it to the lowest possible level.

Carbopol Homopolymer Toxicology Studies

The following tests were performed on powdered Carbopol homopolymers:

Human Repeated Insult Patch Tests

Carbopol homopolymer was impregnated into a 1" X 1" square piece of surgical gauze and moistened with 0.2 mL distilled water just prior to application to the skin of 54 human volunteers.

In order to evaluate the skin irritation and sensitization potential of this product, a series of 12 applications was conducted with each panelist

*Final Assessment Report of the Safety of Carbomers-934, -910, -934P, -940, -941 and –962 Journal of the American College of Toxicology, Vol. 1, No. 2, 1982, pp. 109-141.

during the primary/induction phase. On four consecutive days of weeks 1, 2 and 3, the patch containing the test material was applied to its designated site. The patches were removed and the contact sites were examined 24 hours after each application. Following a one week rest period (week 4) a challenge phase was conducted on week 5 with 4 applications of the test material on a virgin site of each volunteer.

Carbopol homopolymer produced no visible effect in 41 subjects out of 54 during the primary irritation/activation period. Faint or moderate reddening of the skin occurred on one occasion in 10 subjects, 2 times on one subject and 4 times on another subject. These effects would put Carbopol homopolymer in the category of a weak skin irritant. Two subjects out of 53 displayed solitary episodes of faint or moderate reddening in the challenge phase; however, the investigators concluded they did not display a sensitizing reaction.

It was concluded that the results furnish no basis for contraindicating skin contact with Carbopol homopolymers under similar or less stringent conditions than the testing conditions used.

Skin Irritation

The skin irritation potential of Carbopol homopolymer was evaluated in rabbits in accordance with FHSA regulations. Each of six rabbits received a 0.5g dose of the test article as dermal application to both an intact and abraded test site. The dose was held in contact with the skin under a semi-occlusive binder for an exposure period of 24 hours. Following the exposure period, the binder was removed, and the remaining test article was wiped from the skin using gauze and distilled water. The test sites were subsequently examined and scored for dermal irritation for up to three days following patch removal.

Although slight well-defined erythema (redness of the skin) was noted at 25 hours, all responses had subsided by the 72 hours observation. No edema (swelling) was noted at any test site.

Under the test conditions, Carbopol homopolymer is considered a slight irritant to rabbit skin. The calculated Primary Irritation Index for Carbopol homopolymer is 0.58.

Eye Irritation

The eye irritation potential of Carbopol homopolymer was evaluated. A standard amount, 0.1g (or 0.1 mL of the dilute solution) of the test material was administered to groups of six albino rabbits. The respective test material was instilled into the conjunctival sac of one eye of the test animals while the other eye served as a control. The eyes were not washed after instillation. A similar procedure was followed on an additional three animals, with the exception that saline rinse was used.

In the no-rinse group, Carbopol homopolymer produced minimal conjunctivitis in 6 of 6 test animals at 24 hours. Redness and swelling persisted to the study termination (7 days) in 4 of 6 rabbits. Similar responses were seen in the rinse group.

It was concluded that Carbopol homopolymer was not considered to be an eye irritant (rabbit) based on the no-rinse group according to FHSA evaluation criteria.

Carbopol ETD-Series Polymer Toxicology Studies

The toxicology studies summarized below were performed on 2 lots of experimental polymers with chemical compositions representative of the Carbopol ETD polymer family. Therefore, the toxicology data below is expected to be valid for the commercial grades of Carbopol ETD and EZ-2 polymers.

Human Repeated Insult Patch Tests

Two lots of the dry experimental Carbopol ETD polymers were impregnated separately into 20mm X 20mm X 1" surgical gauze pads which were moistened with distilled water just prior to application to the skin of 98 human volunteers in order to evaluate its skin irritation and sensitization potential. A series of 12 applications was conducted with each panelist during the primary/induction phase. On four consecutive days of weeks 1, 2 and 3, the patch containing the test material was applied to its designated site. The patches were removed and the contact sites were examined 24 hours after each application. Following a one week rest period (week 4), a challenge phase was conducted on week 5 with 4 applications of the test material on a virgin site of each volunteer.

Neither lot of Carbopol ETD polymer produced any product-related effects in any of the subjects during the primary irritation/activation or challenge period.

The investigator concluded that the results furnish no basis for contraindicating skin contact with Carbopol ETD polymers under similar or less stringent conditions than the testing conditions used.

Skin Irritation

The skin irritation potential of 2 lots of experimental Carbopol ETD polymers was evaluated undiluted and as a 1% neutralized solution in rabbits according to international OECD guidelines. The test material (0.5g of dry polymer or 0.5 mL of 1% neutralized solution) was applied to the intact skin on each of three animal backs. The dose was held in contact with the skin under a semi-occlusive binder for an exposure period of 4 hours. Following the exposure period, the binder was removed, and the remaining test article was wiped from the skin using tap water and paper towels. The test sites were subsequently examined and scored for dermal irritation for up to seven days following patch removal.

Although very slight erythema (redness of the skin) and edema (swelling) were noted with the undiluted lots, all responses had subsided by the day 7 observation. Very slight erythema also was noted with one lot of the 1% test solution. However, even with this lot, the observation was limited to one of the tree animals and was only seen at the 4 hour observation.

Under the test conditions, Carbopol ETD polymers would be considered a slight irritant to rabbit skin when undiluted (Primary Irritation Index 0.9 - 1.5), and a non-irritant to a very slight irritant when tested as a 1% solution (Primary Irritation Index 0.0 - 0.1).

Eye Irritation

The eye irritation potential of 2 lots of experimental Carbopol ETD polymer was evaluated undiluted and as a 1% neutralized solution according to international OECD guidelines. A standard amount of the test material (0.1 mL or the weight equivalent, 0.04 g) was administered to groups of three albino rabbits. The respective test material was instilled into the conjunctival sac of one eye of the test animals while the other eye served as a control. The eyes were not washed after instillation.

Under the test conditions, Carbopol ETD polymers (undiluted) produced slight to moderate corneal irritation, and conjunctival irritation which cleared by the study termination (day 7). Only slight iridal and conjunctival irritation was noted with the 1% solution and all irritation was found to clear by 72 hours.

NOTE: The 1% solutions were neutralized to pH 6.9-7.0.

Global Inventory Status

The status of powdered Carbopol polymers on the various worldwide chemical inventories is indicated in the following chart.

Chemical Inventory	Carbopol® Polymers As A Class
United States TSCA	Yes
European Economic Community EINECS	Yes*
Canada DSL	Yes
Japan MITI	Yes
Australia AICS	Yes
Korea KICS	Yes

*These products are polymers. EINECS does not list polymers, only monomers. The monomers in these products are listed on EINECS.

Harmonized tariff system classification for powdered Carbopol products is 3906.90.

Food Contact Regulations

It is the interpretation of Lubrizol Advanced Materials, Inc. that Carbopol homopolymers, as polyacrylic acids, are currently satisfactory for use under portions of the following Food Contact Regulations, when used consistent with these regulations:

173.310[2] "Boiler Water Additives"
173.340[3] "Defoaming Agents"
175.105[4] "Adhesives"
175.300[3] "Resinous and Polymeric Coatings"
175.320[3] "Resinous and Polymeric Coatings for Polyolefin Films"
176.170[3] "Components of Paper and Paperboard in Contact With Aqueous and Fatty Foods"
176.180[2] "Components of Paper and Paperboard in Contact with Dry Foods"
176.200[2] "Defoaming Agents Used in Coatings"
177.1210[5] "Closures with Sealing Gaskets for Food Containers"

The following regulation, 177.2260, is understood to allow for the use of Carbopol polymers:

177.2260[4] "Filters, Resin-Bonded" – Provided Carbopol polymer is used in combinations with polyvinyl alcohol.

It should be noted that most of the above regulations have extraction requirements on the finished product that must be met before final clearance can be obtained. These clearances do not apply to Carbopol ETD or Carbopol EZ polymers.

Carbopol Polymers As Pesticide Ingredients

Carbopol homopolymers and copolymers are currently satisfactory for use under the following EPA pesticide regulation:

Regulation 40CFR 180.1001. "Exemptions from the Requirements of a Tolerance" lists those substances (inert or occasionally active) which are exempted from tolerance used in pesticides applied to raw agricultural products. Carbopol polymers are included in paragraphs (c), (d) and (e) of this EPA regulation in the following manner.

40CFR 180.1001 9(c). Pesticide formulations applied to growing crops or to raw agricultural commodities after harvest list –

"Polymer derived from the following monomers: acrylic acid, sodium form; butyl acrylate, ethyl acrylate; … "Carbopol polymer neutralized with NaOH to form the sodium salt would fit the description of a polymer of acrylic acid, sodium salt."

40CFR 180.1001 (d). Ingredients in pesticide formulations applied to growing crops only includes acrylic acid, polymerized and its ethyl and methyl esters. Acrylic acid polymerized would describe unneutralized Carbopol polymers.

40CFR 180.1001 (e). Ingredients in pesticide formulations applied to animals includes polyacrylic acid. This describes unneutralized Carbopol polymers.

All three paragraphs limit the use of Carbopol polymers as "surfactants, related adjuvants or surfactants".

Therefore, powdered Carbopol polymers could be used under 40CFR 180.1001 paragraph (c) if neutralized with NaOH to form the sodium salt and under paragraphs (d) and (e) as the product is sold.

Heavy Metals

Powdered Carbopol polymers are in compliance with all CONEG Model Toxics Legislation; Carbopol polymers do not exceed 100 parts per million by weight of lead, cadmium, mercury or hexavalent chromium. To the best of our knowledge, Carbopol polymers do not contain arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver or zinc.

[2] As the sodium salt of Carbopol polymer (sodium polyacrylate)
[3] As the sodium salt of Carbopol polymer (polyacrylic acid, sodium salt) for use as a stabilizer and thickener in defoaming agents containing dimethylpolysiloxane in an amount usually required to accomplish the intended effect.
[4] As the sodium salt of Carbopol polymer (sodium polyacrylate) for use only: 1.) as a thickening agent of natural rubber latex coating, provided it is used at a level not to exceed 2 percent by weight of coating solids, or 2.) as a pigment dispersant in coatings at a level not to exceed 0.25 percent by weight of pigments.
[5] Carbopol polymer in combination with polyvinylalcohol

Lubrizol Advanced Materials, Inc. does not:

- use any of these heavy metals in the manufacture of powdered Carbopol polymers.
- expect any of these chemical substances to be produced as a result of our manufacturing processes, or
- routinely test for the presence of these substances (due to the first two responses).

Periodic testing has indicated the following (under the following detectable limits):

Pb	<0.1 ppm
Hg	<0.5 ppm
Sb	<0.5 ppm
Cd	<0.5 ppm
Ni	<1.0 ppm
Total heavy metals (As lead)	<20 ppm

Ozone Depleting Substances (ODS)

According to the definitions provided in the final ruling published as 40 CFR part 82 on February 11, 1993, polymers do not contain, nor are manufactured with ozone depleting chemicals.

ISO 9000 Registration

The Carbopol polymer manufacturing locations worldwide have achieved ISO 9002 registration. ISO 9000 is a system for establishing, documenting and maintaining a system for ensuring the quality of the results of a manufacturing process.

Chemical Manufacturers Association (CMA)

Lubrizol Advanced Materials, Inc. is a member of the CMA. As a member, Lubrizol has firmly adopted the Responsible Care Initiative. This Initiative is the most ambitious and comprehensive health, safety and environmental improvement effort ever attempted by an American industry.

Responsible Care commits all members to two critical elements:

- to continually improve performance in the areas of health, safety and environmental quality, and
- to work with the local communities to elicit and respond to public concerns about products and operations.

Lubrizol Advanced Materials, Inc. ensures that its chemical products are designed, manufactured, marketed, distributed, stored, used and/or disposed of safely without adverse effect to human health or the environment.