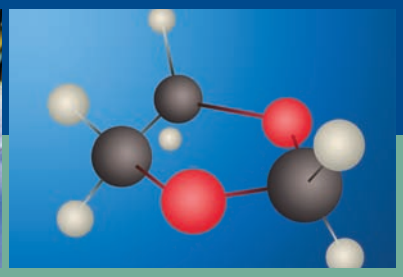
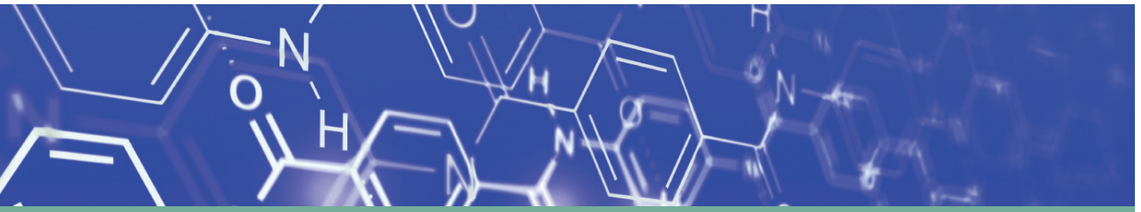
1,3-Dioxolane

- **Coatings** – Maximize water & solids, minimize %VOC
- **Polymers** – Co-monomer for POM's; Solvent for oxygenated polymers
- **Reaction Solvent** – Strong Solvent for Organometallics
- **Cleaning** & paint & photoresist removal

NOVOLYTE technologies



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For contact information go to www.novolyte.com

Novolyte Technologies is the former Fine Chemicals Division of Ferro Corp.

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OSR-140

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ISO 9001:2000

1,3–Dioxolane

Strong solvency, a great tox profile, and low cost cure a lot of problems for formulators who use 1,3-dioxolane. Regulatory and increased performance requirements have led to dioxolane's choice for replacement of NMP, ketones, and halogenated solvents in coatings, photoresists, and inkjet inks.

This cyclic reaction product of ethylene glycol and formaldehyde can exhibit behavior typical of ethers or acetals as conditions dictate. While not as chemically stable as Novolyte Glycol Diethers, under near-neutral conditions, dioxolane is used as a reaction solvent. It is completely miscible with water and all common organic solvents.

Acidity enhances dioxolane's reactivity: for example, it hydrolyzes under mildly acidic conditions and polymerizes under the influence of strong acid catalysts.

Dioxolane also reacts photochemically. Like other ethers, dioxolane forms peroxides on exposure to air, but it does not exhibit the tendency to accumulate peroxides to dangerously high levels.

Whether as solvent or reagent, whether for new or existing application, Novolyte's dioxolane meets rigid standards set for industries that cannot tolerate impurities. The physical, chemical and applications information contained in this brochure can help you decide whether dioxolane meets your requirements also.

Applications I

Dioxolane Is A Strong Aprotic Solvent

Dioxolane is increasingly used in the formulation of water-borne coatings. While a VOC itself, dioxolane maximizes the amount of solids and water due to its high solvency and water solubility.

When a chemical reaction involves either an organic salt, or an organo-metallic compound or even some inorganic salts, dioxolane should be evaluated as a candidate solvent. The orientation of its two oxygen atoms influences the rate and selectivity of chemical reactions in ways that are different from other solvents. In addition to its important use with organometallics, its strong solvent characteristics are useable in many reactions which do not involve metals, particularly polymer reaction systems and coatings. Dioxolane is rapidly finding acceptance as a replacement solvent for methylene chloride, 1,2-dichloroethane, 1,1, 1-trichloro- ethane and methyl ethyl ketone. However, one must remember that in contrast to the chlorinated solvents, dioxolane is water soluble and highly flammable.

The following physical properties can be used in considering dioxolane as an alternative to other solvents, especially when safety or cost- effectiveness is an issue:

	4-Me-1,3-Dioxolane	Diethyl Ether	Methylene Chloride	Tetrahydrofuran	1, 1, 1-Trichloroethane	**Dioxolane**	Methyl Ethyl Ketone	Ethylene Dichloride	Monoglyme	Dioxane	Toluene	Methyl Cellosolve
MW	8.81	74.1	84.9	72.1	133	74.1	72.1	99.0	90.1	88.1	92.1	76.1
BP(°C)	86	34.5	39.8	65.7	74.1	75.6	79.6	83.4	85.2	101.3	110.6	124.5
Vapor Press (20°C,mmHg)		440	350	145	100	70	71	65	50	27	22	6.2
Freezing Pt. (°C)		-116	-97	-108	-33	-95	-86	-35	-69	11.8	-95	-85
Flash Pt. (°C)	-2	-45	None	-17	None	-6	-5	-9	-6	+12	+4.4	+46
Density (g/ml)(20°C)	0.983	0.714	1.32	0.888	1.34	1.067	0.806	1.26	0.868	1.034	0.866	0.965
Viscosity (cP)(25°C)	0.7	0.23	0.43	0.50	0.77	0.60	0.39	.67	1.1	1.3	0.57	1.7
Dielectric Constant		4.2	11	7.5	7.0	7.34	18	10	5.5	2.2	2.4	17
Dipole Moment		1.2	1.6	1.6	1.8	1.5	2.8	2.1	–	0.4	0.4	2.0
Specific Ht. (cal/g)		0.54	0.29	0.41	0.26	0.38	0.53	0.30	0.44	0.42	0.39	0.53
Ht. of Vapor (cal/g)		84	79	95	60	114	118	85	74	99	99	123
Evap. Rate (butyl acetate=1)	5	11.8	14.5	6.3	6.0	3.5	5.8	5.1	4.0	2.2	2.0	0.53
Solubility, water in, %		1.3	0.14	100	0.03	100	9.9	0.16	100	100	0.03	100
Solubility, in water, %	6.0	1.32	100	0.09	100	22.6	0.87	100	100	100	0.05	100
Solubility Parameter, ($cal/cm^3)^{1/2}$		7.7	9.9	9.5	8.8	10.2	9.3	10.2	8.4	10.0	8.9	12.1
Hydrogen Bonding Group	M	M	P	M	P	M	M	P	M	M	P	S

Solubilility Of Polymers In Dioxolane

Polymers produced from polar monomers are very susceptible to softening or dissolving in dioxolane. Traditionally, chlorinated solvents were used extensively for materials such as polycarbonates, acrylates, cellulosics, urethanes, phenolics, nitriles, urea formaldehydes, alkyds, etc. However, dioxolane is finding increasing use in these and other polymer systems such as polyesters, vinyls, epoxys, and halogen-containing polymers.

A dye solution containing an acrylate copolymer, a nigrosine dye and an alkyd can be held together with dioxolane to form a tight bonding film to polyester and acrylates. Solutions for casting films of cyanoethylated carbohydrates are prepared in dioxolane.

A vesicular phenoxy resin can be prepared in a special quaternary ammonium or phosphonium salt solution containing dioxolane. Urea and phenol-formaldehyde resins have extended pot life when prepared in dioxolane.

Dioxolane is efficient when used to bond high acrylonitrile polymers to themselves.

Dioxolane is uniquely the material of choice to plasticize polyacrylamide so that the material can be formed into useful objects. PVC will also dissolve in dioxolane.

The laminate of a heat sealable textile sheet material shows improved resistance to laundering at elevated temperatures when formulated with dioxolane. Crease resistant cellulosic fabrics are obtained by treatment with a crosslinking agent containing dioxolane. Pretreating polyester fibers with dioxolane gives improved dye retention.

Because of its proclivity for solublizing polymers, dioxolane can be used in paint, film, and photoresist removers. Removal of a crosslinked alkyd resin is achieved within 30 minutes of applying dioxolane.

Metal Working And Electroplating

In this application area, dioxolane functions primarily as a polymer or matrix interaction product. The product obtained by reaction with acetylenic alcohols is useful as a brightening additive in nickel electroplating. Dioxolane allows for surface control in tin-lead electroplating systems. Addition of dioxolane to a mineral acid etching solution increases the effectiveness of the solution. Use of polydioxolane in the electro-deposition of copper produces bright, highly ductile, low stress, good leveling copper deposits.

Applications I

Organometallic And Inorganic Systems

The compatibility of dioxolane with organometallic compounds leads to many commercial applications. When 5 g. of dioxolane in one gallon of gasoline is used in conjunction with 0.125 g. of cyclopentadienyl manganese, hydrocarbon emissions are reduced from 200 to 145 ppm. Pesticidal compositions containing metal salts of pentachlorophenol and hydroxyl amines can be made in high concentrations with dioxolane, and then diluted with water without precipitating the active ingredients.

Alkali metal salts of phenols and oximes can be formulated with dioxolane to produce a cream that will protect the user against the effects of mustard gas. Butadiene is cyclotrimerized in the presence of an alkoxytitanium compound and dioxolane. In contrast to failure of a THF based Grignard reaction on a pentafluoroaromatic nitrile to produce the desired para substitution, replacement of the THF with dioxolane produced the desired compound.

Like most ethylene glycol based ethers, dioxolane dissolves certain inorganic salts. Dioxolane works well in magnesium perchlorate systems for manufacturing semipermeable membranes. LiBH4 is quickly and quantitatively prepared from NaBH4 and lithium halide in dioxolane. The formation of clear oil solutions of overbased alkaline earth sulfonates is promoted by dioxolane. Dioxolane serves as part of a solvent package when formulating electrolyte solutions for use in electrical capacitors, for WO3 based electrochromic cells, and for an electro-chemical system which causes hydrogen to dissolve in palladium.

Lithium Batteries

The benefits of working with dioxolane when compounding lithium battery electrolyte solutions (organic) have been widely recognized since the early days of lithium systems. However, dioxolane has a tendency to polymerize cationically during cell use. Over the years, numerous methods were devised to eliminate this problem. Conversely, this polymerization characteristic can be used to prepare a solid organic polymer electrolyte.

It is well known that for optimum performance, particularly conductivity, or to meet special performance requirements, various solvents are blended. A striking example of solvent synergism occurs with dioxolane and monoglyme. There are hundreds of patents and publications covering the use of dioxolane in blends with other solvents.

The cell chemistry of dioxolane and the effect of trace contaminants has been the subject of several publications over the years, particularly because of its value in secondary (rechargable) systems. In rechargables, dioxolane imparts high cycling efficiency and conductivity, and decreases polarization of the anode during the charging cycle. Several recent publications highlight the unique value of dioxolane in secondary batteries.

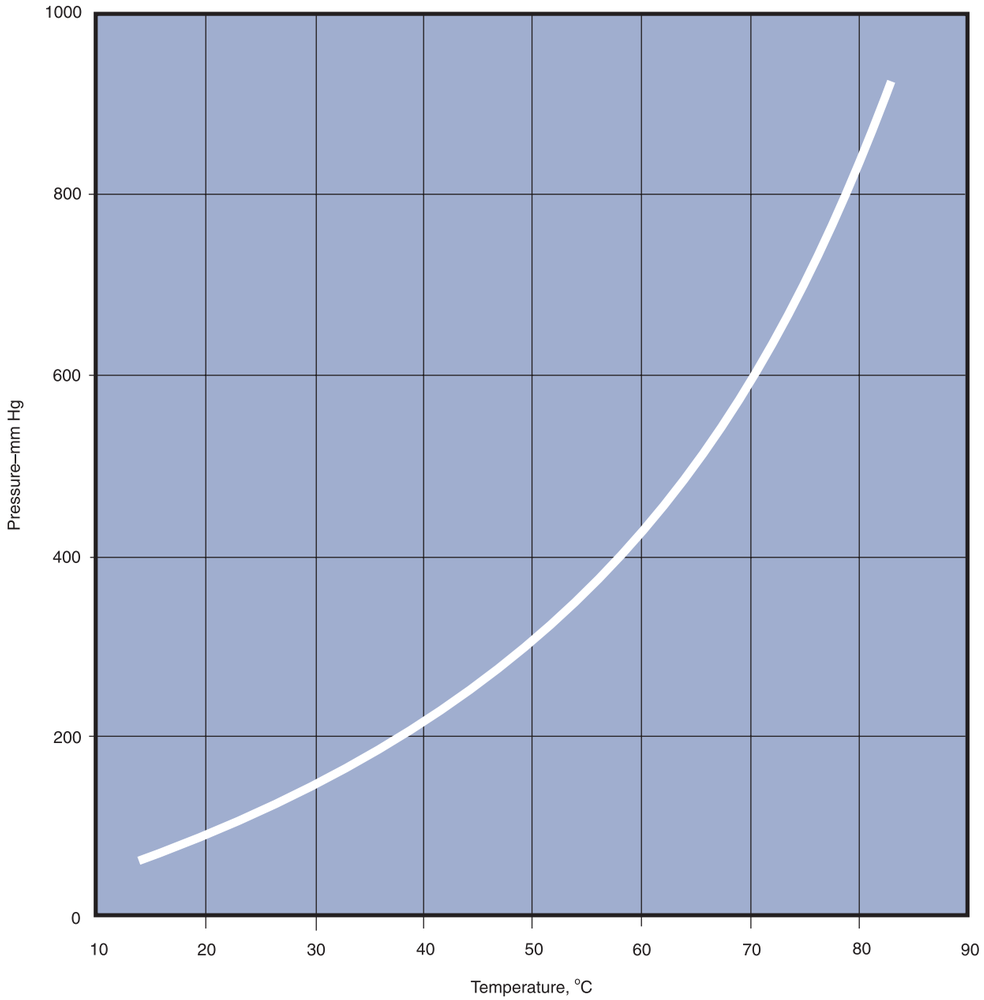
Dioxolane can be used to prepare lithium ion carbon anodes.

Miscellaneous Applications

Dioxolane is effective in a number of miscellaneous applications. Dioxolane is an oxygenate for gasoline, that effectively increases octane number. Similarly, dioxolane will increase the cetane number of diesel fuel while raising the pour point and decreasing the gel temperature – for winter driving and diesel storage

Dioxolane is a solubilizing agent in phenolic resin foams. It is an effective solvent for dissolving and removing tar and asphaltines in the petroleum industry. Dioxolane can be nitrated to form an energetic plasticizer for propellants and explosives. Chlorinated solvents can be stabilized against metal-induced decomposition by use of dioxolane. It can serve as an absorption agent for NOx in a combustion gas scrubber.

Vapor Pressure Temperature Relationship

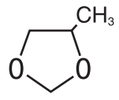


New Developments

Novolyte Technologies is capable of producing other acetals. Sample qualities of dioxepane and 4-methyl dioxolane are available for evaluation. Both compounds are on the TSCA Inventory.

In addition, if you need production quantities of other acetals, contact one of Novolyte's technical representatives to discuss your requirements.

1,3-dioxepane
B.P. 119°C
CAS. NO. 505-67-7



4-methyl dioxolane
B.P. 86°C
CAS. NO. 1072-47-5

Applications II

Use Of Dioxolane As A Reactant

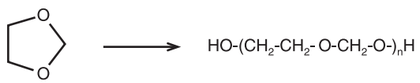
Although dioxolane is primarily known as a solvent, or as an inhibitor in 1,1,1- trichloroethane, it is not widely recognized that this molecule undergoes numerous chemical transformations to produce many interesting and useful molecules. Some of these reactions are highly distinctive and specific.

Homo- And Copolymerization With Aldehydes

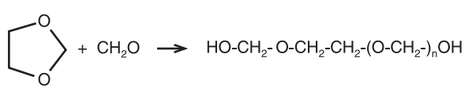
There are many publications on dioxolane's use as a monomer or co-monomer in the formation of polyacetals. We can only describe here the basic chemistry and selectively cite a few publications.

Most polymerizations involving dioxolane, either with itself or with aldehydes and ethers, proceed via a cationic mechanism, using strong Lewis acids such as BF_3-etherate, SbF_5, $HClO_4$, CF_3SO_3H, AsF_5, etc.

For homopolymerization:



Used as a comonomer with formaldehyde to produce stable POM's – Polyoxymethylene:



It is also used as a co-monomer with formaldehyde homologs such as tetraoxane, 1 ,3,5 trioxane and trioxepane. Dioxolane can copolymerize with THF. To prepare polyacetals with improved lubricating properties, dioxolane can be oligomerized with stearaldehyde, then mixed with a high MW trioxane-dioxolane copolymer. Cationically active polydioxolane when mixed with polystyrene will form grafts with no gel.

Participation In Various Polymer Systems

Dioxolane is used in the photoinitiation of styrene and in the cationically catalyzed copolymerization with styrene. Maleic anhydride is polymerized in the presence of dioxolane via a radical mechanism to give a viscous oligomer with dioxolane end groups. However, maleic anhydride and dioxolane in the presence of benzoyl peroxide is claimed to polymerize via a cationic mechanism.

When used as part of the initiation system, dioxolane allows narrow, controlled MW distribution in the production of vinyl ether polymers.

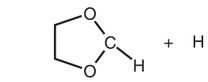
Dioxolane can serve as a MW regulator in the polymerization of vinyl chloride. It can also serve to stabilize crosslinked PVC.

Cellulose ester graft copolymers are prepared by treating cellulose acetate with dioxolane.

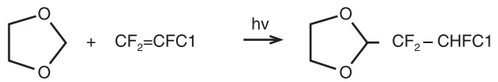
Modification of a titanium catalyst with dioxolane will produce alternating copolymers between conjugated diolefins and monoolefins.

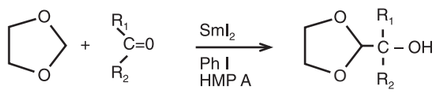
Doubly Activated Methylene

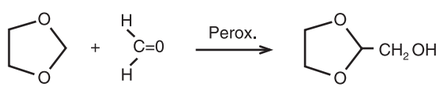
The methylene flanked by two oxygens is susceptible not only to oxidation, but also to radical abstraction of a hydrogen leading to addition of the following elements across a double bond:

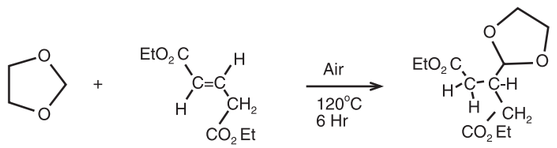


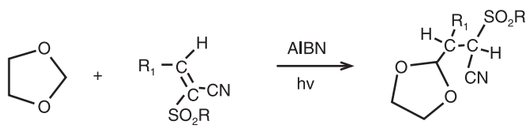
Some examples are shown below.





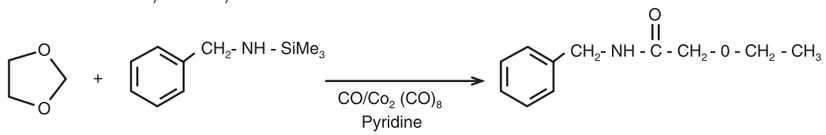


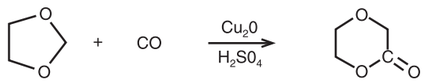




Carbonylation

Dioxolane is easily carbonylated.





Handling, Health & Safety

General Handling

Since dioxolane is a powerful solvent for many polymers, selecting materials which can contact it in a process can be difficult. Teflon is highly resistant, and substances such as butyl rubber, polyethylene and polypropylene can be used in many applications. Resistance to dioxolane is improved when polymer molecular weight is high or there is a high degree of crosslinking or crystallinity. Specific applications should be tested for polymer swell, softening, degradation and permeability.

Carbon steel can be used for storing and handling pure dioxolane. We recommend storage in an inert atmosphere such as nitrogen to assure product purity for a prolonged period. In this way, both oxygen and atmospheric moisture can be avoided. Contact with acids should be avoided since this will lead to hydrolysis of the dioxolane. Formaldehyde release is usually not a problem since the primary products of hydrolysis are hemi-acetals. However, the potential for some formaldehyde release should be kept in mind when designing a process which involves contact with acids.

Dioxolane does not biodegrade in standard laboratory tests. However, due to its susceptability to oxidation and to hydrolysis of the acetal functionality, it is not likely that it will accumulate in nature.

Recovery And Recycle

Novolyte can provide technical information to help customers develop a safe and cost-effective recycle program. In some cases, Novolyte can also provide final "back-to-specs" purification services at the Baton Rouge plant location, if needed. Please contact a service representative if you need this type of service.

Peroxides

Novolyte maintains high purity standards by a number of rigid manufacturing controls. Dioxolane is manufactured in a dry, inert environment and is packaged under nitrogen. This assures product integrity over long periods of storage. Our studies show that peroxide concentration is barely detectable in the ppm range even after storage periods as long as a year.

Peroxides in ethers can decompose to form other impurities. However, unlike ethers such as THF and ethyl ether where peroxides accumulate rapidly, dioxolane peroxides are much more labile and tend not to build to high levels. Safe decomposition of peroxide in dioxolane can be accelerated simply by warming the dioxolane under nitrogen to 65°C for a brief period.

In many instances where dioxolane is used, air exposure cannot be avoided. In these cases, peroxide concentration should be monitored, since peroxides could form undesirable chemical by-products in the system.

With some chemicals there is a tendency for peroxides to become isolated by phase separation which results in the formation of a high peroxide layer. This phenomenon is unlikely in dioxolane because of the very high solubility of peroxides and other oxygenated organic material in dioxolane.

Peroxide formation is effectively stopped by using a phenolic antioxidant such as BHT. Novolyte dioxolane contains 75 ppm BHT unless otherwise specified.

We know of no incident due to peroxide buildup in dioxolane. However, the highest standards of safety, product stewardship and responsible care should be maintained when using and recycling dioxolane.

Acute Toxicity

Various publications have listed oral LD50 values for 1,3-dioxolane ranging from 3,000 to 7,600 mg/kg in rats. Lethal concentrations for inhalation exposures (4 hours) were found to be 87, 166, and 118 g/m3 for rats, guinea pigs, and rabbits, respectively. The dermal LD50 value was determined to be 15 g/kg. Intoxication symptoms, including reduced gain in body weight, reduced blood acetyl-cholinesterase and disturbances in the neuromuscular system, have been observed at 1/10 the intragastric LD50 of 5.8 g/kg. Other toxic endpoints evaluated, including total protein, albumin, bilirubin, urea, and activities of alanine and aspartate aminotransferase, alkali phosphatase, and succinic dehydrogenase in blood, indicate no significant ($P<0.05$) toxic effects at this level of exposure. No cumulative toxic effects were observed in acute toxicity studies.

Subacute Toxicity

A 13-week inhalation study involving rats exposed to 0, 300, 1000, or 3000 ppm dioxolane in air showed a reversible reduction in white blood cell counts in animals exposed to 1000 and 3000 ppm levels. A no observed effects level of 300 ppm for rats was established in this study.

Cytotoxicity

Cytotoxicity was indicated by an increase in the level of micronucleated polychromatic erythrocytes in bone marrow when rats were given two doses of dioxolane ranging from 1.5 to 6 g/kg on consecutive days. However, negative results have been reported in a study of five histidine-requiring strains of salmonella typhimurium indicating an absence of mutagenicity for dioxolane, with and without activation by liver microsomes. Negative results were also demonstrated in studies involving the Chinese Hamster Ovary test. An assay of dominant lethal mutations in the germ cells of male rats indicate no difference between control and experimental groups using oral or inhalation routes of exposure. Focal necrosis of semeniferous epithelium and alteration of spermatogenesis was found in some subjects at doses greater than 0.58 g/kg.

Developmental Toxicity

Animal testing did not show developmental toxicity at high doses. Exposure of rats to 10 or 20 percent of the LD50 concentration of dioxolane via intragastric or inhalation routes caused no increases in pre- or post-implantation fetal losses. Exposure of rats throughout pregnancy to either 0.01, 0.02, or 0.10% dioxolane in drinking water, or to 125 ppm dioxolane in air for 6 hours per day, 5 days per week, demonstrated no significant differences between control and experimental groups with respect to mating, fecundity, male-female fertility indices, gross external pup abnormalities, number of pups delivered, pup survival, and maternal body weight.

Summary

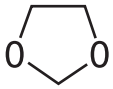
The current data supports the position that dioxolane is a solvent of low toxicity. However, in keeping with standard practices for the handling of organic solvents, certain precautions should be taken. Skin contact should be avoided to reduce the possibility of irritation. Adequate ventilation should be employed to minimize inhalation hazards and guard against the concentration of flammable vapor. For further information, contact the Health and Safety Manager, Novolyte Technologies.

Customer Service: Customerservice@novolyte.com

NOVOLYTE technologies

GO GREEN!

With Novolyte 1,3–Dioxolane



Strong Solvency

Water Soluble

Good for modifying the surface of polar polymers and films

Excellent Tox Profile

NOVOLYTE technologies

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