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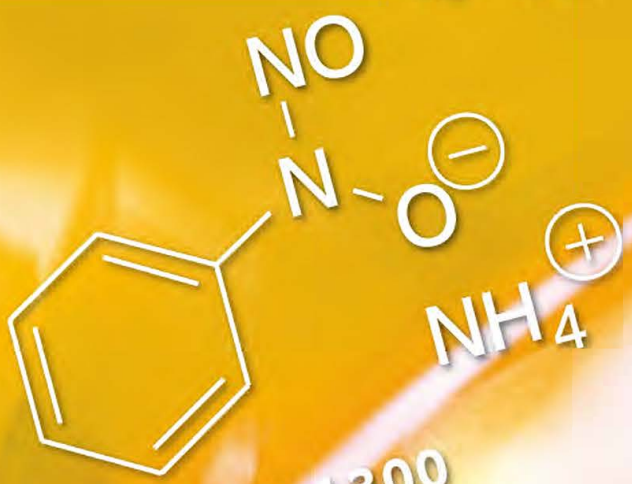
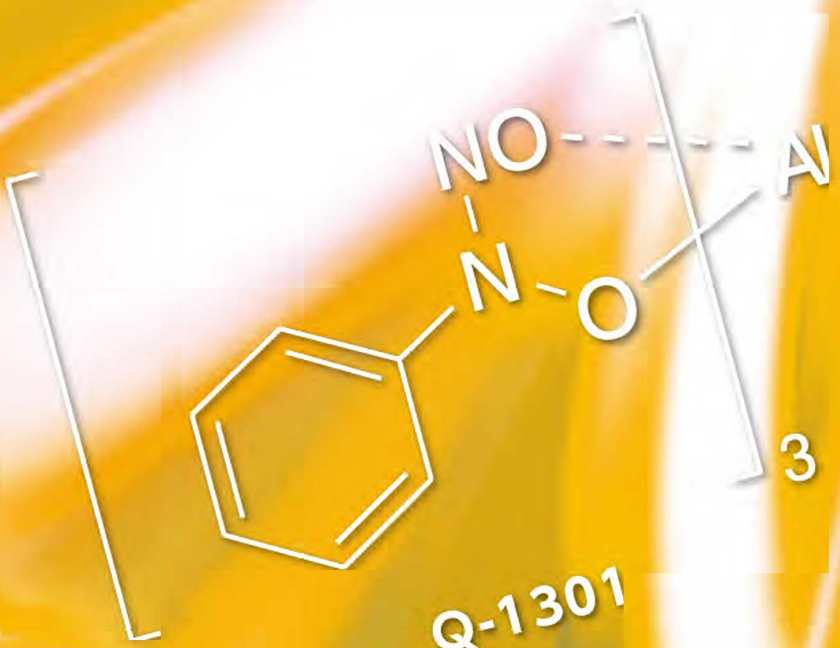
Wako

High Performance Polymerization Inhibitors

Q-1300 , Q-1301



Q-1300



Q-1301

Characteristics

- Strong polymerization inhibiting effect even with at low concentration.
- Monomers can be safely stored for long periods.
- Effective as preservation stabilizers of composition for photo-radical polymerization.
- Provide strong polymerization inhibiting effect in an oxygen-free environment.

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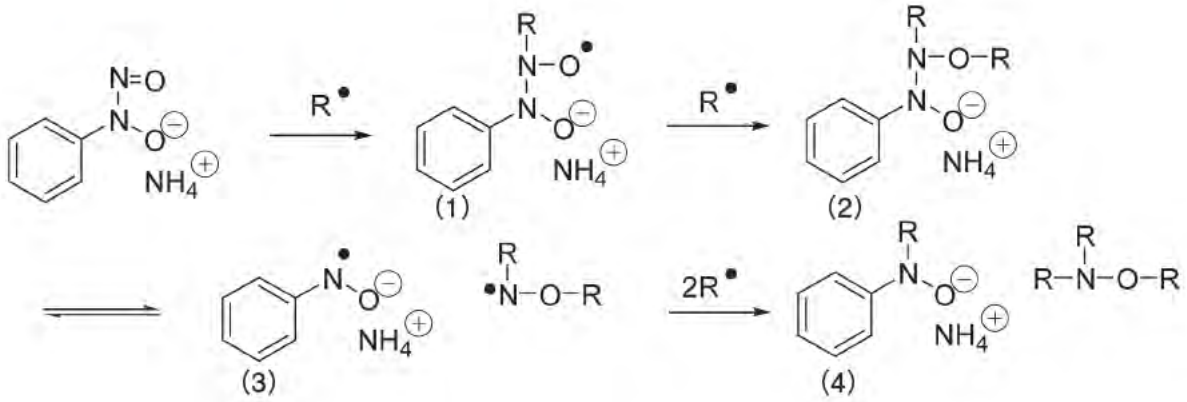
Introduction

Polymerization inhibitors are reagents which are used to prevent undesirable polymerization by light or heat. Conventional polymerization inhibitors, such as hydroquinone, are at a disadvantage because they cannot prevent polymerization under certain conditions. By contrast, high-performance polymerization inhibitors Q-1300 and Q-1301 show a strong polymerization inhibiting effect when purifying or storing highly reactive monomers regardless of conditions. Since Q-1300 is water-soluble, and Q-1301 is oil-soluble, these are applicable for different monomers.

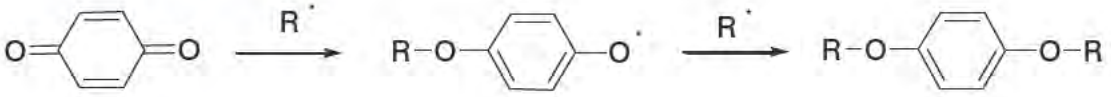
Mechanism of Polymerization Inhibition (Presumed)

In the cases of Q-1300 and Q-1301

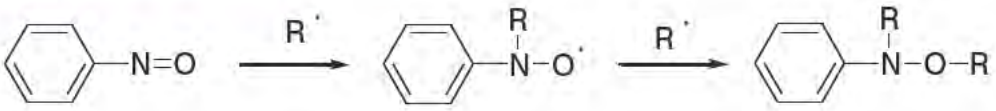


The nitroso group catches a radical in the system, and (1) is formed.
Attack of (1) to monomer causes a reaction with propagating radical to form a stable coupling product (2).
N-N cleavage of coupling product (2) proceeds at the temperature of 50°C or higher and forms a product (3).
Furthermore, the product (3) reacts with 2 radicals to form a product (4).

In the case of benzoquinone [1)]



In the case of nitroso compounds [2)]



Comparison of Polymerization Inhibiting Effects

Measurement conditions

- Purified styrene
- Concentration of polymerization inhibitor: 1,000 ppm
- Heating temperature: 120°C
- Under nitrogen gas flow

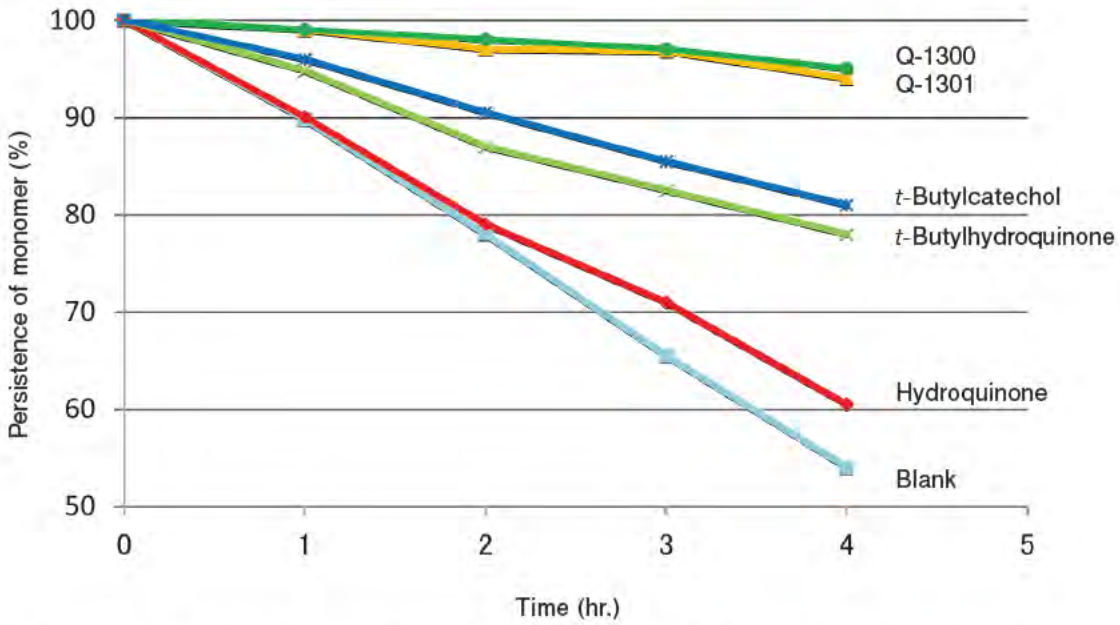


Figure-1: Persistence of monomer (%) under the existence of different polymerization inhibitors

⇒ Q-1300 and Q-1301 show stronger polymerization inhibiting effect than other polymerization inhibitors at high temperature.

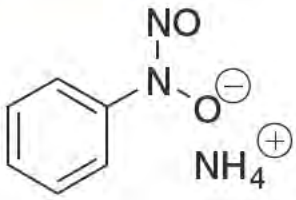
Examples of Applications

- Preservative stabilizer (monomers, UV inks, UV paints, and photosensitive resins).
- Prevention of polymerization during distillation of monomers.
- Prevention of polymerization during production of monomers and oligomers, and during heating/mixing of monomers.
- Suspension of polymerization when an abnormal polymerization is observed.
- Suspension of polymerization once the target polymerization rate is attained.

Q-1300 Water soluble

Chemical name	Ammonium *N*-Nitrosophenylhydroxylamine (cupferron)

Structural



Formula	$C_6H_9N_3O_2$
Molecular weight	155.16
CAS No.	135-20-6
Appearance	White-slightly yellowish brown, Crystalline powder
Melting point	140–144°C (dec.)
TSCA	Listed
EINECS	Listed

Recommended addition amount

10～50 ppm

Packaging 500 g , 5 kg

Solubility

(g/solv. 100 g、10℃)

Water		Methanol	DMF
8.7	9.7 (30℃)	4.4	0.8

Change with time

Simple Q-1300, after being stored at any temperature, was measured for appearance in its solid state, decomposition temperature and the colored extent in a 1% aqueous solution. When storing it, 5w/w% of ammonium hydrogen carbonate was added as a stabilizer, which was put in another air permeable container.

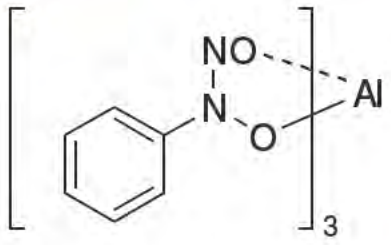
Temperature	10°C or less				37°C			
Item	Appearance	Decomposition temperature (°C)	Status of water solution	APHA	Appearance	Decomposition temperature (°C)	Status of water solution	APHA
(Day) 0	Slightly yellow powder	141.5	Almost clear	15	Slightly yellow powder	141.5	Almost clear	15
10						141.6		
25						142.4	Very slightly cloudy	20
40					Slightly brown crystalline powder	141.8		40
50						141.6		50
60					Light brown crystalline powder	141.9	Slightly cloudy	120
120					—	—	—	—

※APHA : American Public Health Association Reference standard for measurement of water color

Q-1301 Oil soluble

Chemical name	*N*-Nitrosophenylhydroxylamine aluminium

Structural



Formula	$C_{18}H_{15}AlN_6O_6$
Molecular weight	438.33
CAS No.	15305-07-4
Appearance	White-light yellowish brown powder
Melting point	160°C or higher
TSCA	Listed
EINECS	Listed

Recommended addition amount

10～50 ppm

Packaging

1 kg , 5 kg

Solubility

(g/solv. 100 g、20℃)

Chloroform	THF	Toluene	Methanol
97	86	23	0.4

Change with time

Simple Q-1301, after being stored at any temperature, was measured for appearance in its solid state, melting point, content and the colored extent in a THF solution.

Temperature	10℃					35℃				
Item	Appearance	Melting point (°C)	Content (%)	Status of THF solution	APHA	Appearance	Melting point (°C)	Content (%)	Status of THF solution	APHA
(Month) 0	Almost white powder	169.1	99.8	Clear	100	Almost white powder	168.3	99.9	Clear	100
3		169.1	100.0		150		168.1	98.8		120
6		168.8	99.9		150		167.8	97.5		150
9		169.0	99.9		150	–	–	–	–	–
12		169.2	99.8		150	–	–	–	–	–

Thermal Polymerization Inhibiting Effect

Q-1300 and Q-1301 show an excellent inhibiting effect in thermal polymerization.

Acrylic acid [3)]

The formation level of polymerized product was comparatively-measured based on the change of relative viscosity of the solution which was heated for a certain period of time under the existence of polymerization inhibitor.

Measurement conditions

- 50% Acrylic acid water solution, polymerization inhibitor concentration of 1,000 ppm/monomer
- Heating temperature: 100°C
- Heating time: 8 hours
- Under nitrogen gas flow

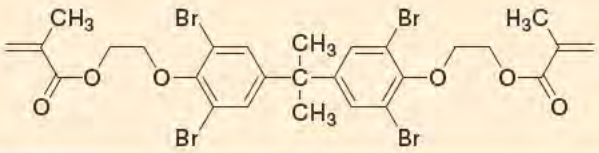
Relative viscosity of acrylic acid water solution before and after heating

Polymerization inhibitor	Relative viscosity (30°C)
No addition, before heating	1.77
Hydroquinone monomethyl ether	Unmeasurable because of high viscosity
Q-1300	1.77

Polyfunctional vinyl monomer [4)]

The thermal stability of polyfunctional vinyl monomer composition was measured.

Composition of monomer

	60 part
Divinylbenzene	20 part
Chlorostyrene (o-/p- = 65/35)	20 part

Measurement conditions

- Heating temperature: 70°C

Comparison of thermal stability

Polymerization inhibitor	Addition amount (ppm)	Result
Blank	—	Increase of viscosity after 5 hours
Hydroquinone monomethyl ether	500	Increase of viscosity and gelation after 3 hours
Q-1301	5	No increase of viscosity and gelation, even after 15 hours

Polymerization Inhibiting Effect in Distillation (Heating and Reduced Pressure)

Q-1300 and Q-1301 show an excellent inhibiting effect in distillation (heating and reduced pressure).

Acrylic acid [5]

The inhibiting effect of the product when used for purification of acrylic acid by distillation was measured.

Measurement conditions

- Acrylic acid: 1 L
- Distillation temperature: 103°C/20 kPa

Comparison of polymerization inhibiting effect

Polymerization inhibitor	Addition amount (ppm)	Result
Manganese acetate Hydroquinone monomethyl ether	500 200	Formation of polymerized product was observed in the container and the distillation column after approximately 300 ml of distillate was obtained.
Manganese acetate Q-1300	20 20	Formation of polymerized product was not observed.

Dimethylaminoethyl methacrylate [6]

The effect of polymerization inhibitor was measured when synthesizing dimethylaminoethyl methacrylate by transesterification reaction, followed by separation and purification by distillation.

Measurement conditions

[Transesterification reaction]

- Methyl methacrylate: 750 g (7.5 mol)
- Dimethylaminoethanol: 268 g (3.0 mol)
- Pb: 12.4 g (0.06 mol)
- Reaction temperature: 65-70°C
- Reaction time: 4.5 hours

[Purification by distillation]

- Distillation temperature: 72°C/2.4 kPa — 63.5°C/0.7 kPa

Comparison of the inhibiting effects in transesterification reaction

Polymerization inhibitor	Addition amount (g)	Yield (%)	Residue (g)	Remark
Hydroquinone monomethyl ether	3.0	—	—	Polymerizing during reactions
Q-1300	2.3	91.5	13.2	

Radical Polymerization Inhibiting Effect

Vinyl chloride

During polymerization of vinyl chloride, stirring and cooling were stopped, and the change in temperature over time was measured after the addition of polymerization inhibitor.

Measurement conditions

- Vinyl chloride: Water = 1: 1.2, PVA 0.08%
- Radical polymerization initiator: V-65 (0.03%)
- Polymerization temperature: 56.5°C
- Q-1300: 100 ppm
- After five hours of polymerization, stirring and cooling in the system were stopped, and the polymerization inhibitor was added one minute later.

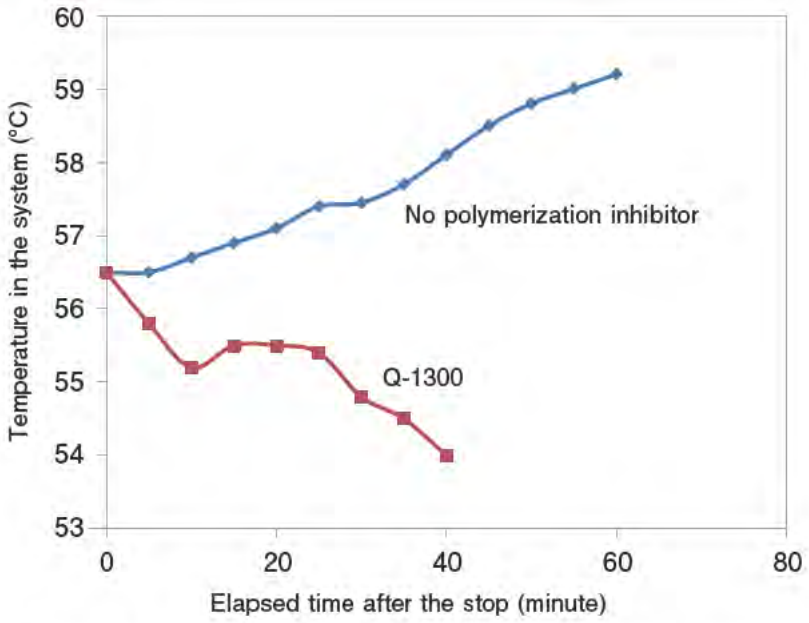


Figure-2: Polymerization inhibiting effect by polymerization inhibitor

⇒ Q-1300 **has an excellent inhibiting effect** in suspension polymerization.

Measurement of the Induction Period of Radical Polymerization

Sodium acrylate

The inhibiting effect of polymerization inhibitor in the water solution polymerization of sodium acrylate was evaluated.

Measurement conditions

- Monomer concentration: 20% (w/v)
- Polymerization inhibitor: 2,000 ppm/monomer
- Radical polymerization initiator for water solution: V-50 (0.4%/monomer)
- Polymerization temperature: 50°C

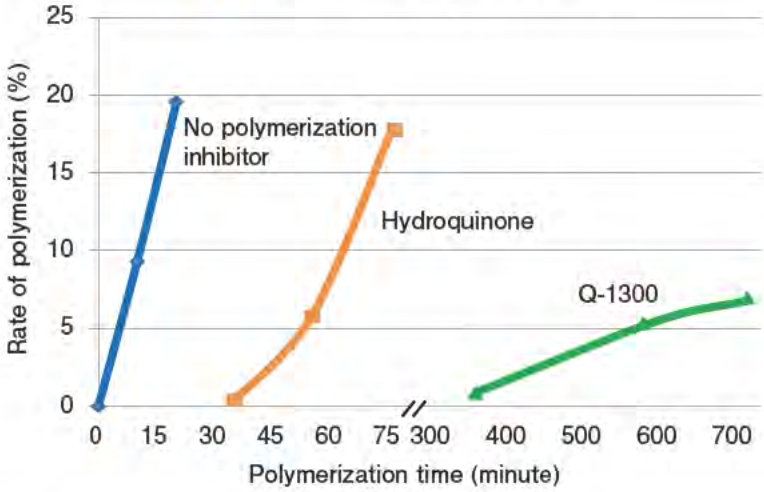


Figure-3: Induction period and inhibiting effect by polymerization inhibitor

Acrylamide

The inhibiting effect of polymerization inhibitor in the water solution polymerization of acrylamide was evaluated.

Measurement conditions

- Monomer concentration: 50% (w/v)
- Polymerization inhibitor: 2,000 ppm/monomer
- Radical polymerization initiator for water solution: V-50 (1.0%/monomer)
- Polymerization temperature: 50°C

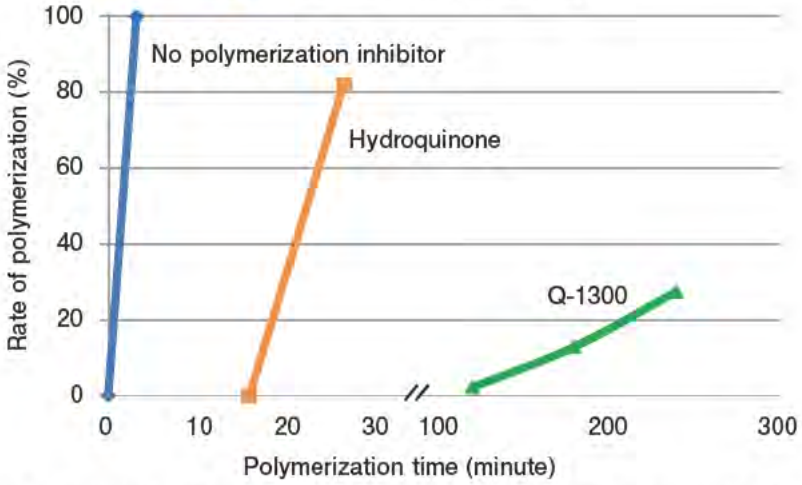


Figure-4: Induction period and inhibiting effect by polymerization inhibitor

⇒ Q-1300 **has a longer induction period and a stronger inhibiting effect** as compared with other polymerization inhibitors.

Propagation Inhibiting Effect in the Case of Abnormal Polymerization

The product inhibits propagation of popcorn polymer* and shows a higher inhibiting effect than other inhibitors.

* Popcorn polymer: Generic name of less soluble and less meltable polymers formed by three-dimensional crosslinking of monomers during distillation.

Glycidyl methacrylate [7)]

We compared the growth of popcorn polymers under the condition of existence of polymerization inhibitor in the glycidyl methacrylate polymerization system.

Measurement conditions

- Glycidyl methacrylate: 30 part Methyl acrylate: 20 part Water: 1,500 part
- Polymerization inhibitor: 1,000 ppm/monomer Polymerization temperature: 35°C Polymerization time: 10 hours
- Polymerization initiator: APS-Na_2SO_3 Water-based redox polymerization

Inhibiting effect in the case of abnormal polymerization

Inhibitor	Polymerization yield	Specific viscosity of polymer	Remark
Blank	87.3	0.124	Popcorn monomer 2.7 part formed
Q-1300	92.7	0.122	No popcorn polymer formed

Acrylic acid [8)]

Nucleus of popcorn polymer (SBR) was placed in the gas phase under the reflux condition of acrylic acid, and the change of mass of the popcorn polymer was measured.

Measurement conditions

- Reflux under reduced pressure (6.7 kPa), reaction time: 6 hours

Inhibiting effect in the case of abnormal polymerization

Inhibitor	Addition amount (ppm)	Change of mass of popcorn nucleus (%)
Phenothiazine	126	+636
Q-1300	102	0.0

Methyl methacrylate [8)]

Nucleus of popcorn polymer (SBR) was placed in the gas phase under the reflux condition of methyl methacrylate and the change of mass of the popcorn polymer was measured.

Measurement conditions

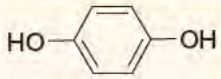
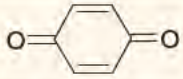
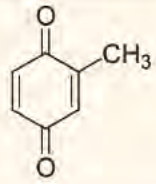
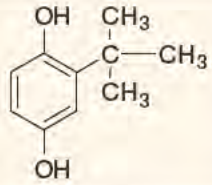
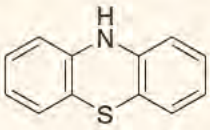
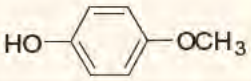
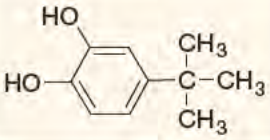
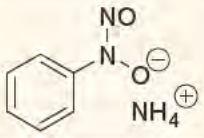
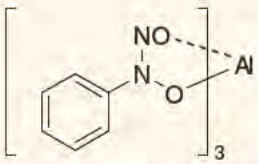
- Reflux under reduced pressure (6.7 kPa), reaction time: 6 hours
- The inhibitor was divided into six parts and added each part every an hour.

Inhibiting effect in the case of abnormal polymerization

Inhibitor	Addition amount (ppm)	Change of mass of popcorn nucleus (%)
Phenothiazine	The same mole quantity as that of Q-1300	+237
Hydroquinone	The same mole quantity as that of Q-1300	+243
Q-1300	100	+18

List of Related Items

2014.9.17

Structural formula	Product Name	Product code	Packaging	Remark
	Hydroquinone	085-01212	25 g	
		089-01215	500 g	
	*p*-Benzoquinone	171-00242	25 g	
		175-00245	500 g	
	2-Methyl-1,4-benzoquinone	353-00382	25 g	
	*t*-Butylhydroquinone	027-07212	25 g	This product is also available in bulk.
		021-07215	500 g	
	Phenothiazine	165-24142	25 g	
		169-24145	500 g	
	*p*-Methoxyphenol	084-01282	25 g	
		088-01285	500 g	
	4-*t*-Butylpyrocatechol	026-10852	25 g	
		020-10855	500 g	
	cupferron (Q-1300)	032-04902	25 g	
		034-04901	100 g	This product is also available in bulk.
		036-04905	500 g	
	N-Nitroso-N-phenylhydroxylamine Aluminium Salt (Q-1301)	143-04562	25 g	This product is also available in bulk.
		147-04565	500 g	

Reference documents

1) J.C. Bevington, N.A. Ghanen, H.W. Melville, *Trans. Faraday Soc.* 51 346(1995) ; *J. Chem.Soc.* 1955 2822
2) Polymer Bulletin 33,325-329(1980)
3) Japan Examined Patent Application Publication No. Sho-39-220 Nitto Rikagaku Kogyo Co., Ltd.
4) JP-A-Sho-63-170401 Toray Industries, Inc.
5) EP 301879(1989) Hoechst Celanese
6) JP-A-Sho-52-153912 Nitto Chemical Industries Co., Ltd.
7) Japan Examined Patent Application Publication No. Sho-48-2934 Kanegafuchi Chemical Industry Co., Ltd.
8) USP 4772740(1988) Mallinckrodt