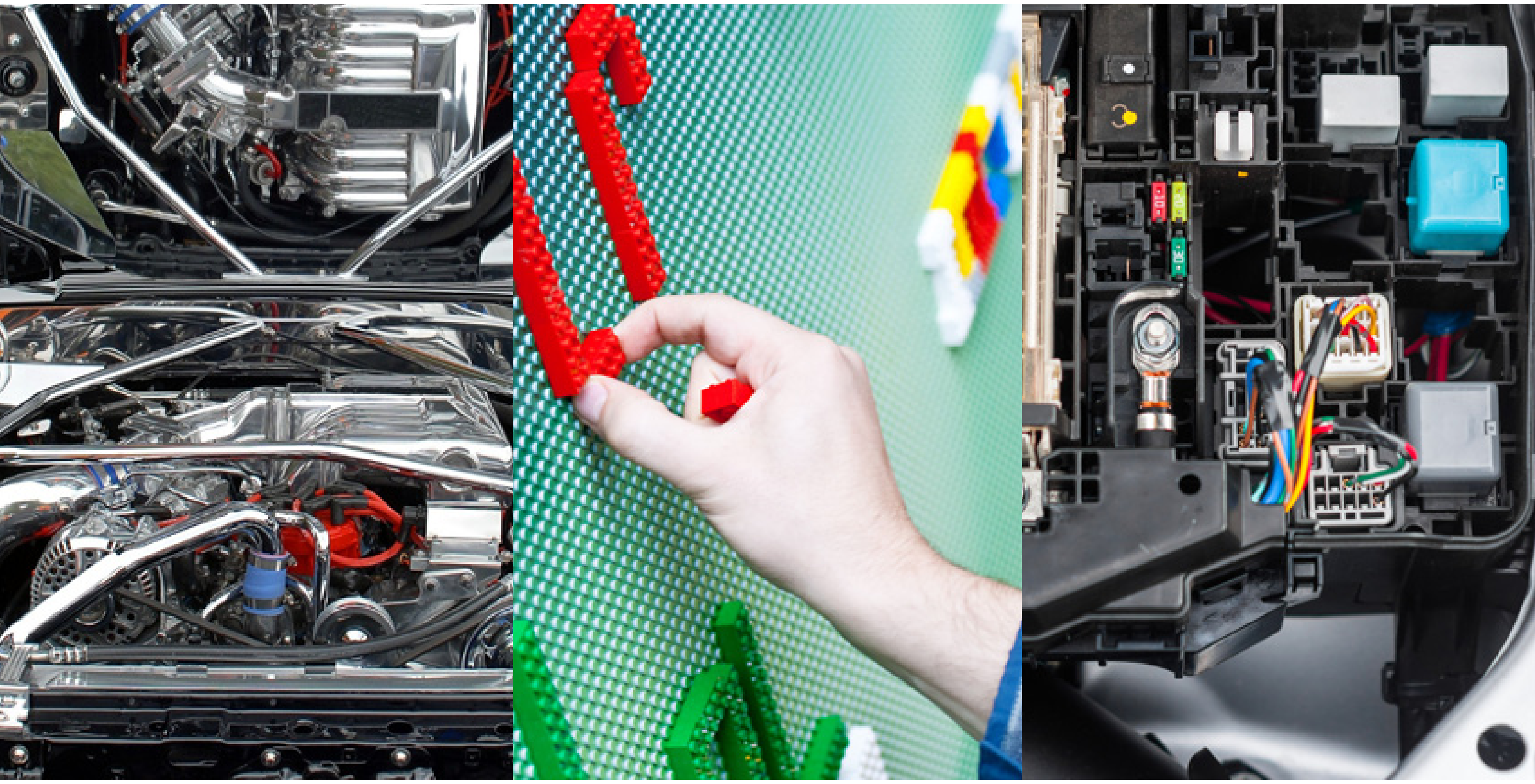
Vertellus

Smart Chemistry. Our Specialty.™

Topanol®



Topanol CA Antioxidant for Polymers

PLASTICS & POLYMERS

Contents

'Topanol' CA as an antioxidant for polymers

'Topanol' CA antioxidant is a high molecular weight hindered phenolic antioxidant. It is used primarily in polymer systems that are sensitive to thermal and oxida-tive degradation because of free radical and peroxide formation.

'Topanol' CA will provide excellent protection against degradation at high processing temperatures and will extend the service life of polymers that are used at elevated temperatures. The original grade of 'Topanol' CA was developed some 40 years ago and has gained an excellent reputation in the polymer industry.

An improved grade 'Topanol' CA-SF has also been developed which is approximately 10% more active than the original grade and has improved handling and storage benefits. Details are given of suitable usage levels and of the effects that may be expected in polyolefins, styrenics, plasticisers, hot-melt adhesives, SBR latices, polyamides and polyesters.

'Topanol' CA is highly efficient, has low volatility, does not stain and has wide toxicological clearance. Hence it is useful in polymers intended for a very wide range of end uses. Its high efficiency can be enhanced by using it with other antioxidants such as phosphites and thioesters, which produce synergistic effects, leading to very effective and economical formulations.

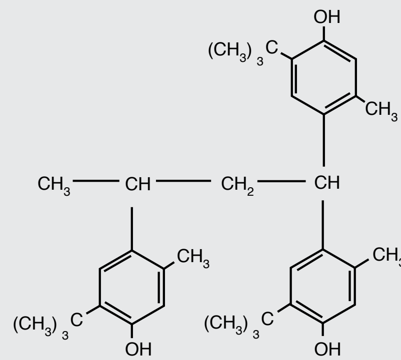
The form in which 'Topanol' CA is used most often is as free running powder for blending with polymers in granular or powder form. For some applications, however, its use as an aqueous dispersion is more convenient.

Availability of aqueous dispesions is subject to minimum order quantities. However, formulations to make any of the above aqueous dispesions are available on request.

What is 'Topanol' CA?

'Topanol' CA antioxidant is 1,1,3-tris (2-methyl-4-hydrox-5-tbutyl phenyl) butane, a condensation product of 3-methyl-6-tert-butyl phenol and crotonaldehyde.

Its structure may be represented as:



The benefits of using 'Topanol' CA antioxidant

- 'Topanol' CA provides effective protection against thermal oxidative degradation at low usage levels in a very wide range of polymers.
- 'Topanol' CA exhibits excellent synergy with many secondary antioxidants.
- 'Topanol' CA can be incorporated in a wide range of polymeric systems.
- 'Topanol' CA is non staining.
- 'Topanol' CA is easily dispersed in polymer systems because of its free-flowing properties as a powder.
- 'Topanol' CA may be prepared as an aqueous dispersion, alone or with suitable synergistic secondary antioxidants convenient for addition to e.g SBR/ABS latexes prior to drying.
- 'Topanol' CA gives long-lasting protection because of its low volatility.
- 'Topanol' CA has gained wide approval in food contact applications.
- 'Topanol' CA has good extraction resistance to water and petroleum jellies (used in cables)

Applications

It has already been noted that 'Topanol' CA can be used effectively as an antioxidant in a wide range of polymer systems. The following notes indicate usage levels and the corresponding performance in many such systems. They are not exclusive; other systems may be treated and other levels-of-use may be adopted. Final decisions about precise formulations for particular applications should be based on suitable development programmes for which Vertellus Specialties Inc. will be pleased to offer advice and assistance.

Recommendations are given for suitable starting points, based on wide laboratory and manufacturing experience.

Low density polyethylene (LDPE)

LDPE is used in a very wide range of applications with a corresponding range of required properties, both in processing and in end-uses. Wherever there is a need for resistance to oxidation, 'Topanol' CA is a suitable antioxidant. It may be used alone or in conjunction with thioesters which produce a powerful synergistic effect, greatly increasing the life stability of the polymer.

Process stability

High process temperatures have the general effect of increasing Melt Flow Index (MFI) and hence making fabrication processes (extrusion, injection moulding, film extrusion) more difficult to control. Table 1 shows the significant effect that the addition of a low concentration of 'Topanol' CA has on this increase. An additional advantage is that, unlike other antioxidants (BHT for example) 'Topanol' CA will not produce a yellow discolouration of the polymer during processing or during storage as reeled film. Table 2 compares the performance of two competitive antioxidants with that of 'Topanol' CA used alone and with a typical synergist such as DLTDP.

Table 1 - The effect of 'Topanol' CA on the Melt Flow Index of LDPE

Antioxidant	Melt Flow Index (190^{O}C/10kg)	
	Before processing	After[(a)] processing
None	2.8	36.0
'Topanol' CA, 0.01%	3.4	9.4

(a) Processing for 60 minutes in a Brabender Plastograph mixing head at 160°C

Table 2 - Changes in Yellowness Index of LDPE on multiple extrusion at 200^{O}C

Antioxidant	Yellowness Index *(b)*	
	After 1 extrusion	After 4 extrusions
'Topanol' CA, 0.1%	3	4
'Topanol' CA, 0.05% +		
DLTDP, 0.15%	3	4
Product B, 0.1%	8	13
Product C, 0.1%	13	29

(b) A higher index indicates a more yellow sample

Life stability

Where a long service life is required, or where oxidation may be accelerated by high temperatures or by the presence of transition metals, 'Topanol' CA, alone or combined with DLTDP, is recommended. As an indication, Table 3 shows the improvement achieved in high temperature stability and compares it with that given by two other antioxidants.

Table 3 - The temperature stability of LDPE resins containing 'Topanol' CA as an antioxidant

Antioxidant	Oven stability hours (c) at		
	105°C	120°C	140°C
None	15	5	1.8
'Topanol' CA, 0.1%	242	67	5.6
'Topanol' CA, 0.05% + DLTDP, 0.15%	207	249	26.4
Product B, 0.1%	51	60	5.4
Product C, 0.1%	163	163	11.8

(c) The time to catastrophic degradation of the LDPE specimen

Table 4 - The effect of 'Topanol' CA on the embrittlement time of LDPE containing carbon black, 3%

Antioxidant	Embrittlement time (hours) at	
	120°C	140°C
None	120	29
'Topanol' CA, 0.2%	605	120
'Topanol' CA, 0.03% + DLTDP, 0.06%	1055	270
'Topanol' CA, 0.05% + DLTDP, 0.15%	2010	625

LDPE filled with carbon black

'Topanol' CA is not so susceptible to deactivation by carbon black as are other phenolic antioxidants. For this reason, where PE filled with carbon black is to be stabilised, for example, for cables or water pipes, 'Topanol' CA is particularly recommended. Systems containing 'Topanol' CA in conjunction with a thioester synergist are very effective. Table 4 shows the effects of these systems based on 'Topanol' CA.

LDPE as cable insulation

'Topanol' CA is particularly suitable for use in LDPE intended for use as electrical insulation for copper-containing conductors. It gives excellent antioxidant protection to the cable insulation in the presence of copper ions. Thioester synergised formulations will perform well, as will the combination of 'Topanol' CA with metal deactivators. Table 5 gives some typical performance levels obtained in tests on 0.5mm plaques, compression moulded around copper gauze and aged in an air circulating oven at 105°C.

Table 5 - The degradation of LDPE resins, containing 'Topanol' CA, moulded around copper gauze

Antioxidant	Ageing time (days) at 105°C
None	3
'Topanol' CA, 0.1%	6
'Topanol' CA, 0.1% + DLTDP, 0.03%	30
'Topanol' CA, 0.1% + OABH, 0.1%	44
'Topanol' CA, 0.1% + Product S, 0.1%	74
Product B, 0.2%	17
Product C, 0.2%	9

Cross-linked polyethylenes

In cross-linked polyethylenes, 'Topanol' CA is an efficient antioxidant that may be incorporated before or after grafting. Table 6 shows that, in either case, the polymer system can match the heat ageing requirements of BS 5468:1977 (less than 25% change in tensile strength and elongation at break).

Ultraviolet stability

Although, like most other phenolic antioxidants, 'Topanol' CA will not act directly as a UV stabiliser, it is fully compatible with benzophenone and hindered amine UV stabilisers (HALS). If a thioester is used as a synergist, however, the use of hindered amines is not recommended. Table 7 gives a typical comparison of the performance of suitable systems with that of unstabilised LDPE.

Recommended formulations

Laboratory work and experience in manufacture suggest that the systems in Table 8 will provide good starting points for the development of antioxidant systems suitable for LDPE.

Table 6 - The effects of 'Topanol' CA on the properties of a cross-linked PE resin (d)

Antioxidant	Effect of ageing at 135°C for 168 hours					
	Tensile strength (MPa)			Elongation(%)		
	Before	After	Change	Before	After	Change
None	15.3	8.1	-47%	340	100	-71%
'Topanol' CA, 0.1% (added post grafting)	15.5	15.5	0	327	307	-6%
'Topanol' CA, 0.1% (added prior to grafting)	16.1	15.5	-4%	395	330	-16%

(d) The resin was a silane cross-linked polyethylene

Table 7 - The effect of 'Topanol' CA on the UV stability of a PE resin

Stabilising system	Time (hours) to C=0(e) index 0.2
None	500
'Topanol' CA, 0.1% + Tinuvin 770, 0.1%	3520
'Topanol' CA, 0.05% +Cyasorb 531, 0.3%	2750

(e) The carbonyl (C=0) index = $100\ d^{-1} \log_{10}(I_0/I_t)$
where d = specimen thickness (μm)
I_0 = Intensity of transmitted light, initially
I_t = Intensity of transmitted light, after time t
The frequency of the light source is $1715 cm^{-1}$

Tinuvin is a trademark of BASF.
Cyasorb is a trademark of CYTEC Industries.

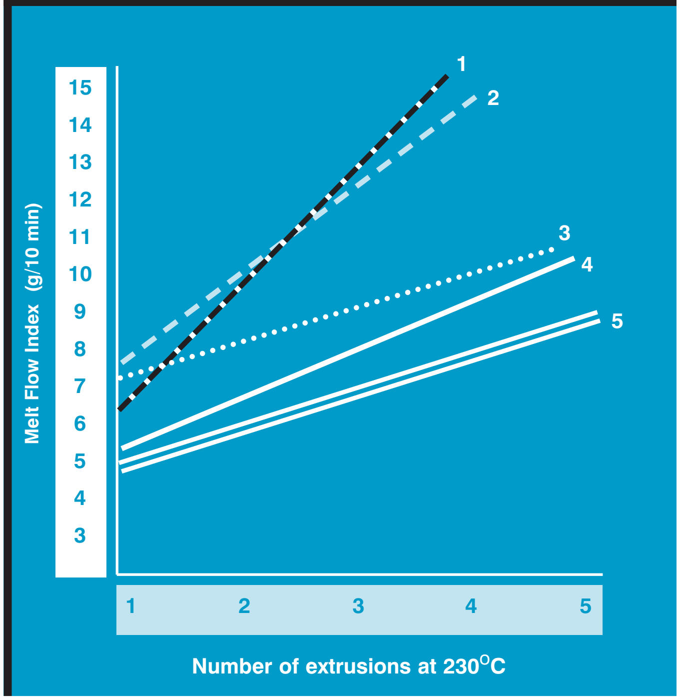
Table 8 - Recommended starting formulations for LDPE

Grade of LDPE	Recommended antioxidant system	
General purpose	'Topanol' CA with thioester or phosphite	0.05% to 0.1% 0.15%
Cable grades	'Topanol' CA with thioester	0.1% to 0.2% 0.3% to 0.6%
	or 'Topanol' CA with metal deactivator	0.1% to 0.2% 0.1%

Polypropylene (PP)

PP is particularly subject to thermal and oxidative degradation because of its tertiary hydrogen atoms. 'Topanol' CA will minimise this degradation during processing at elevated temperatures, including reprocessing scrap material, and will ensure that PP resins retain their physical properties through a long service life. It is recommended that 'Topanol' CA be used in conjunction with a thioester and/or a phosphite synergist for optimum cost effective formulation.

Figure 1 - The effects of 'Topanol' CA on the Melt Flow Index of Polypropylene



Key: Antioxidant content

1. None
2. Product J, 0.1% + DSTDP, 0.25%
3. Product H, 0.1% + DSTDP, 0.25%
4. 'Topanol' CA, 0.1% + DSTDP, 0.25%
5. 'Topanol' CA, 0.1% + DSTDP, 0.05% + Weston 618, 0.05%

Process stability

For efficient fabrication processes, PP must retain good melt flow characteristics. Figure 1 illustrates the excellent performance of 'Topanol' CA as a melt stabiliser for PP in minimising the changes in Melt Flow Index during several extrusions.

Life stability

The thermal stability of PP resins with antioxidant systems that contain 'Topanol' CA is illustrated in Table 9. The samples - 1.25mm thick - were aged in an air circulating oven until they showed signs of brittleness when flexed around a 25mm diameter mandrel. Particularly when used with suitable synergists, 'Topanol' CA increases the time to embrittlement very significantly.

Table 9 - Embrittlement times for PP resins with 'Topanol' CA and other antioxidants

Antioxidant	Embrittlement time(f) at 105°C (hours)
None	24
'Topanol' CA, 0.1%	170
'Topanol' CA, 0.1% + DSTDP, 0.25%	880
'Topanol' CA, 0.1% + Product F, 0.25%	1820
'Topanol' CA, 0.1% + DSTDP, 0.25% + TNPP, 0.05%	1230
'Topanol' CA, 0.1% + Product F, 0.25% + Product G, 0.05%	2860

(f) 1.25mm compression moulded plaques

Changes in colour, as indicated by the Yellowness Index are illustrated in Table 10. Such changes are used as indicators of the onset of degradation and, in addition, colour changes must be minimised for the sake of product appearance. Since the Yellowness Index of an unstabilised sample may be expected to change from 7 to 80 in 24 hours at 135°C, the beneficial effect of the systems incorporating 'Topanol' CA is very clear.

Table 10 - Changes in Yellowness Index of PP on oven-ageing at 135°C and 150°C

Antioxidant	Yellowness Index for the conditions and time shown		
Ageing temperature 135°C (3mm)	Initial	7days	28days
'Topanol' CA, 0.05% + DSTDP, 0.15%	5.9	20.3	27.0
Product H, 0.08% + BHT, 0.1%	14.1	22.5	36.6
Ageing temperature 150°C (1.25mm)	Initial	200 hours	500 hours
'Topanol' CA, 0.1% + DSTDP, 0.25%	7.0	21.1	25.9
'Topanol' CA, 0.1% + DSTDP, 0.25% + TNPP, 0.5%	5.4	17.0	21.5
Product I, 0.1% + DSTDP, 0.25%	5.0	18.6	27.9
Product J, 0.1% + DSTDP, 0.25%	6.3	23.0	32.0

Talc-filled PP

Talc-filled formulations of PP (up to 40% w/w) are commercially important. Because the presence of the filler affects the performance of antioxidants, separate tests have been conducted on antioxidant systems to determine their suitability for such applications. Table 11 illustrates the performance of these systems, showing that there is a marked improvement in performance, whether the PP was aged after a single extrusion or whether a two week immersion in boiling water was also included as a conditioning process.

Table 11 - The resistance to embrittlement of talc-filled PP resins containing antioxidant systems incorporating 'Topanol' CA

Antioxidant System	Time to Embrittlement (hours at 150°C)	
	(g)	(h)
None	24	24
'Topanol' CA, 0.1% + DSTDP, 0.3% + Product K, 0.75%	670	1020
'Topanol' CA, 0.15% + DSTDP, 0.45% + Product K, 1.0%	870	1550
'Topanol' CA, 0.1% + DSTDP, 0.3% + Product L, 1.0%	580	470
'Topanol' CA, 0.15% + DSTDP, 0.45% + Product L, 1.0%	670	700
'Topanol' CA, 0.1% + DSTDP, 0.3% + Product M, 0.75%	550	240
'Topanol' CA, 0.15% + DSTDP, 0.45% + Product M, 1.0%	550	180

(g) Samples - 1.25 mm thick tested after single extrusion

(h) Similar specimens conditioned by 2 weeks immersion in boiling water

Table 12 - The resistance of antioxidant systems to extraction from PP resins by boiling water

Antioxidant system	Days to breakdown on oven ageing(j) after immersion in boiling water for the following number of days				
	0	1	2	4	7
Product H, 0.05% + DSTDP, 0.2%	140	100	117	3	3
Product C, 0.05% + DSTDP, 0.2%	70	20	6	4	3
'Topanol' CA 0.05% + DSTDP, 0.2%	100	70	70	50	3
'Topanol' CA 0.05% + DSTDP, 0.2% + Product N, 0.0125%	90	80	60	50	4
'Topanol' CA 0.075% + DSTDP, 0.2%	80	50	50	20	3

(j) 2.5mm plaques aged at 140°C

Extraction of antioxidant by hot water

Polypropylene is used in many applications where resistance to immersion in hot water is an essential criterion of acceptability. Since many additives, including antioxidants, are extracted by such immersion, with deleterious effects on the subsequent performance of the polymer, a number of antioxidant systems incorporating 'Topanol' CA have been investigated for resistance to extraction. Table 12 shows the results, making it clear that systems incorporating 'Topanol' CA offer considerably longer resistance to extraction.

Ultraviolet stabilisation

'Topanol' CA has been shown to be compatible with benzophenone, benzotriazole and hindered amine UV stabilisers. Phosphite synergists may be used with these stabilisers but thioesters are antagonistic to HALS type stabilisers and their use together is not recommended. Table 13 illustrates the influence of combinations of 'Topanol' CA and UV stabilisers on the reaction of PP resins to UV radiation.

Table 13 - The response to ultraviolet radiation of PP resins containing 'Topanol' CA

Synergistic antioxidant and UV stabiliser added to 'Topanol' CA 0.1%	Time to carbonyl index = 0.06 (hours)
Product O, 0.3%	1220
Product P, 0.15%	2310
DSTDP, 0.25% + Product O, 0.3%	1670
TNPP, 0.25% + Product O, 0.3%	1660
TNPP, 0.25% + Product P, 0.15%	2580

Recommended starting formulations

It is recommended that 'Topanol' CA, with proposed synergists, be evaluated in the grade of polypropylene for which it is intended. However, laboratory and manufacturing experience suggests that the formulations indicated in Table 14 will provide good starting points for development work. Separate adjustment of 'Topanol' CA and of the synergist additives levels, can ensure successful derivation of cost effective formulations.

Table 14 - Recommended starting formulations for PP resins

Antioxidant	Recommended formulations
Good processing and good life stability	'Topanol' CA, 0.1% + DSTDP, 0.25%
Good processing, good colour and fair life	'Topanol' CA, 0.1% + phosphite, 0.25%
Good processing, good colour and good life	'Topanol' CA, 0.1% + DSTDP, 0.25% + phosphite, 0.1%
Light stability (with benzophenone UV stabilisers)	'Topanol' CA, 0.1% + UV absorber, 0.1 to 0.5%
	'Topanol' CA, 0.1% + DSTDP, 0.25% + UV absorber, 0.1 to 0.5%
	'Topanol' CA, 0.1% + phosphite, 0.25% + UV absorber, 0.1 to 0.5%
Light stability (with a hindered amine light stabiliser)	'Topanol' CA, 0.1% + HALS, 0.1 to 0.5%
	'Topanol' CA, 0.1% + phosphite, 0.25% + HALS, 0.1 to 0.5%
Talc-filled PP	'Topanol' CA, 0.1% + DSTDP, 0.3% + Product K, 0.5%
	'Topanol' CA, 0.1% + DSTDP, 0.3% + Product L, 0.1%
Water resistance	'Topanol' CA, 0.05 to 0.1% + thioester, 0.15 to 0.3%

General Note

Since the introduction of PP in the 1950's the production technology has changed significantly. The modern use of high activity catalysts plus the changes in formulations favouring HALS light stabilizers, for example mean that the choices of phenolic antioxidants and synergists are more restricted. Thioesters are generally not recommended for use where HALS light stabilizers are present. In this case phosphites or phosphonites synergists should be used. High levels of non deashed high activity catalysts can give a yellow discolouration when 'Topanol' CA is used, so some caution must be exercised. However, some work with the newer phosphites such as Irgafos® 12 (*Ciba) has shown that the colour formation as measured by the Yellowness Index (Y.I.) is much reduced when compared with the colour formation when the simpler structure phosphites such as Irgafos® 168 are used.
Montell 6501 (*LyondellBasell) resin was passed through an extruder at 230ºC and the Y.I. measured on compression moulded plaques at each pass.

Fig. 1P shows the Y.I. development at the first, third and fifth passes with 'Topanol' CA - SF at 0.05% and the phosphites at 0.10% in each case.

*Irgafos® is a registered trademark of Ciba, now part of BASF.
*LyondellBasell is the successor company to Montell.

Multiple Extrusion of 6501 PP

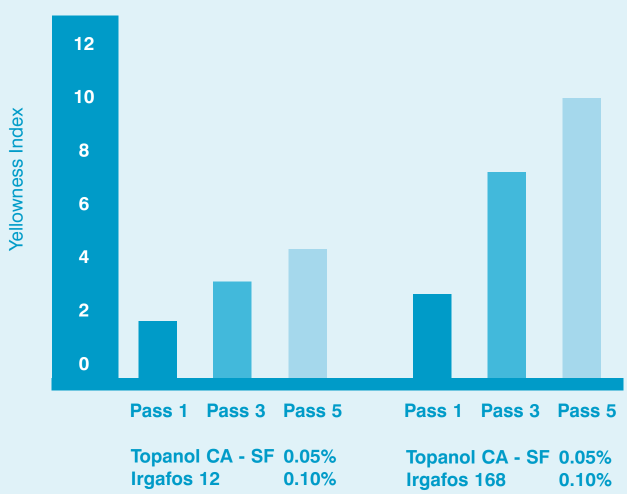


Figure 1P

High Density Polyethylene (HDPE)

'Topanol' CA will stabilise HDPE successfully although there are some limitations to its use. In particular, because 'Topanol' CA has low solubility in paraffinic carrier solvents, it is not generally considered as an additive at the polymerisation stage of the Phillips process. It may, however, be added during compounding. It will successfully protect the polymer during repeated fabrication processes at high temperature and will extend the service life of HDPE products.

Process stability

Table 15 shows that 'Topanol' CA, in small proportions, approximately halves the reduction of the Melt Flow Index of HDPE during repeated extrusion. The effect is particularly marked when 'Topanol' CA is used with synergists such as phosphites or thioesters.

Table 15 - The effect of 'Topanol' CA on the Melt Flow Index of a Phillips type HDPE

Antioxidant system	Melt Flow Index (g/10 min) for extrusion at 240°C	
	1st extrusion	4th extrusion
None	4.8	1.2
'Topanol' CA, 0.02%	6.8	3.8
'Topanol' CA, 0.02% + DLTDP, 0.05%	6.4	4.4
'Topanol' CA, 0.02% + TNPP, 0.05%	7.1	4.4
Product A, 0.02%	5.9	2.8

Life stability

The results of tests on oven-ageing-to-failure are illustrated in Table 16. They show that the stability for formulations containing 'Topanol' CA and a synergist such as DLTDP is very good. Similar results are obtained when 'Topanol' CA is used in conjunction with TNPP.

Table 16 - The temperature stability of HDPE resins containing 'Topanol' CA as an antioxidant

Antioxidant	Time to failure on oven ageing at 140°C (hours)
None	15
'Topanol' CA, 0.05% + DLTDP, 0.2%	1580
Product A, 0.05% + DLTDP, 0.2%	1310

Since polyethylene containing 'Topanol' CA has very low dielectric-loss characteristics, it is recommended for use in electrical applications such as telephone wire insulation. Formulations that incorporate a sulphur-containing synergist such as DLTDP are several times more effective than the traditional sulphur-containing antioxidants commonly used in cable compounds.

The presence of copper, alone or with carbon black, generally reduces the life of HDPE and it is an important feature of formulations containing 'Topanol' CA that they show excellent retention of antioxidant activity in such cases.

Recommended formulations

The level at which 'Topanol' CA should be incorporated depends on the duty for which the HDPE is intended and on the presence of other additives. However, laboratory and manufacturing experience suggests that the formulations indicated in Table 17 will provide good starting points for development work.

Table 17 - Recommended starting formulations for HDPE

'Topanol' CA used alone	0.02% to 0.1%
With a sulphur-containing synergist such as DLTDP the ratio suggested is : 'Topanol' CA : DLTDP = 1 : 3	
If phosphites, such as TNPP are also used the suggestion is : 'Topanol' CA : DLTDP : TNPP = 1 : 2 : 1	

High Impact Polystyrene (HIPS)

Polystyrene itself is relatively resistant towards oxidation and for many applications of crystalline or expandable PS no antioxidant protection is needed. However, rubber-modified polystyrenes are dependent, for their toughness, on components such as polybutadiene. Butadiene rubbers are particularly susceptible to oxidative degradation, with resulting embrittlement and discolouration of the HIPS, but can be protected adequately by 'Topanol' CA, especially when it is used in conjunction with synergists such as thioesters or phosphites. The low volatility of 'Topanol' CA ensures that it is retained during the monomer stripping stage, or during vacuum extrusion, and ensures that the polymer is protected during manufacture, fabrication processes and service.

Process stability

The addition of 'Topanol' CA minimises changes in melt flow index during repeated extrusions. Table 18 compares the performance of 'Topanol' CA and a synergistic system with that of a competitive antioxidant.

Table 18 - The effect of 'Topanol' CA on the Melt Flow Index of HIPS

Antioxidant system	Melt Flow Index (g/10 min) for extrusion at 240°C		
	1st extrusion	4th extrusion	Change (%)
BHT, 0.2%	4.28	5.38	+27
'Topanol' CA, 0.1%	4.36	5.28	+21
'Topanol' CA, 0.05% + DLTDP, 0.1%	4.38	5.36	+22

Life stability

'Topanol' CA is effective both in increasing the length of time before which HIPS becomes embrittled at elevated temperatures and in delaying the onset of discolouration. Table 19, for instance, gives typical performance-improvement levels for several practical blends of antioxidant. they show that 'Topanol' CA, whether alone or in blends, is significantly more effective than "Product A".

Table 19 - Embrittlement times for HIPS resins with 'Topanol' CA and other antioxidants

Antioxidant	Ageing temperature (°C)	Embrittlement time (hours)
None	90	100
'Topanol' CA, 0.03% + TNPP, 0.1%	90	190
Product A, 0.03% + TNPP, 0.1%	90	170
'Topanol' CA, 0.05% + TNPP, 0.15%	90	190
Product A, 0.05% + TNPP, 0.15%	90	310
'Topanol' CA, 0.03% + DSTDP, 0.1%	90	370
Product A, 0.03% + DSTDP, 0.1%	90	180
'Topanol' CA, 0.05% + DSTDP, 0.15%	90	610
Product A, 0.05% + DSTDP, 0.15%	90	320
None	110	100
'Topanol' CA, 0.1%	110	480
Product A, 0.1%	110	140
'Topanol' CA, 0.05% + DLTDP, 0.2%	110	320
Product A, 0.05% + DLTDP, 0.2%	110	320

Ultraviolet stabilisation

'Topanol' CA is compatible with benzophenone, benzotriazole and hindered amine (HALS) UV stabilisers. Many of the blends used as antioxidant systems, because of the effects of synergy, are equally compatible. However, HALS and thioesters react antagonistically and should not be used together in a stabilisation package.

Recommended formulations

Laboratory work and experience in manufacture suggest that the systems in Table 20 will provide good starting points for the development of antioxidant systems suitable for HIPS.

Table 20 - Recommended starting formulations for HIPS

'Topanol' CA	0.1%
'Topanol' CA with DSTDP or DLTDP	0.03% to 0.05% 0.1% to 0.15%
'Topanol' CA with TNPP or phosphites	0.03% to 0.05% 0.1% to 0.15%

Acrylonitrile-Butadiene-Styrene (ABS)

The butadiene rubber in ABS resin is very susceptible to oxidative degradation during manufacture and use of the resin. Such degradation has deleterious effects on both colour stability and embrittlement. The advantages of using 'Topanol' CA as an antioxidant, either alone or with synergists, may be summarised as:

- where a latex process is used to produce a graft ABS resin, the low volatility of 'Topanol' CA ensures that losses of antioxidant caused by volatilisation during drying are minimised;
- the combination of low volatility and high activity of 'Topanol' CA provides protection through repeated processing cycles at high temperatures;
- combined with synergists - such as phosphites and thiodipropionates - 'Topanol' CA gives increased life stability at minimum cost, particularly in demanding applications such as those involving high ambient temperatures.

Process stability

The rubber phase of ABS must be protected against oxidation prior to exposure to elevated temperatures. A technique commonly used to provide this protection is to add 'Topanol' CA to the polymer latex as an aqueous dispersion. It is then intimately dispersed with the rubber particles during coagulation and hence provides maximum protection. In general this technique is more effective than adding antioxidants at the compounding stage since, at that stage, significant oxidation may already have occurred. It is possible to optimise protection by incorporating 'Topanol' CA at both stages, using the dispersion method to stabilise the polymer during drying and adjusting the total antioxidant content by dry compounding to suit particular end-uses. Table 21 compares the increases in Melt Flow Index (MFI) during milling in a Brabender mixing head at elevated temperatures for two formulations containing 'Topanol' CA and for an unprotected control.

Table 21 - The effect of 'Topanol' CA on the Melt Flow Index of ABS

Antioxidant system	Melt Flow Index (g/10 min) after milling at 165°C for		
	10 min	30 min	Change (%)
None	2.84	3.84	+35
'Topanol' CA, 0.2% + + DLTDP, 0.6%	2.88	3.16	+10
'Topanol' CA, 0.2% + TNPP, 0.6%	2.76	2.80	+1

Life stability

Table 22 shows typical values for the increase in the length of time taken to embrittle ABS at 110°C.

Table 22 - Embrittlement times for ABS resins containing 'Topanol' CA as an antioxidant

Antioxidant	Embrittlement time(k) at 110°C (hours)
None	25
'Topanol' CA, 0.1% + TNPP, 0.3%	120
'Topanol' CA, 0.1% + DLTDP, 0.3%	120
'Topanol' CA, 0.2% + TNPP, 0.6%	220
'Topanol' CA, 0.2% + DLTDP, 0.6%	290

(k) Storage time to produce cracking when 0.5 mm plaques are flexed around a 25 mm mandrel

Recommended formulations

Laboratory work and experience in manufacturing suggest that the formulations in Table 23 will provide good starting points for the development of antioxidant systems suitable for ABS.

Table 23 - Recommended starting formulations for ABS

Synergistic antioxidant and UV stabiliser added to 'Topanol' CA 0.1%	Time to carbonyl index = 0.06 (hours)
	DSTDP, DLTDP or TNPP, 0.15 to 0.25%
High impact or High heat resistance	'Topanol' CA, 0.1 to 0.25%, with DSTDP, DLTDP or TNPP, 0.25 to 0.5%

Methyl methacrylate-Butadiene-Styrene (MBS)

The use of 'Topanol' CA will minimise embrittlement and degradation in MBS polymers. Table 24 gives formulations recommended for initial evaluations. They are based on laboratory and manufacturing experience.

Table 24 - Recommended starting formulations for MBS

'Topanol' CA	0.1 to 0.3%
'Topanol' CA	0.1 to 0.2%
with DLTDP or DSTDP	0.2 to 0.45%

Addition of 'Topanol' CA as an aquenos dispersion to the MBS latex prior to drying is particularly recommended as it will provide optimum protection to the resin and reduce the risk of fires in the dryer.

Styrene Butadiene Rubber (SBR)

SBR latex is used in carpet backing, upholstery backing, paper saturation, adhesives, dipped goods and binders. In each of these applications it is subjected to thermal and oxidative degradation leading to embrittlement and discoloration. 'Topanol' CA provides an excellent protection, increased further by incorporating a thioester synergist such as DTDTDP.

Physical Properties

Table 25 shows the time to embrittlement of a series of films of SBR, 0.33mm thick, containing different antioxidant systems. The films were aged at 135°C and tested for brittleness by flexing them around a 25mm diameter mandrel. The table indicates a significant improvement in performance when formulations incorporating 'Topanol' CA were used as.

Table 25 - Embrittlement times for SBR films containing 'Topanol' CA as an antioxidant

Antioxidant	Embrittlement time at 135°C (hours)
None	15
'Topanol' CA, 0.1%	30
'Topanol' CA, 0.1% + DTDTDP, 0.3%	75
Product D, 0.25%	30
Product D, 0.2% + DTDTDP, 0.6%	50

Recommended formulations

For optimum performance, it is recommended that 'Topanol' CA is added as an aqueous dispersion. Laboratory work and experience in manufacture suggest that the systems in Table 26 will provide good starting points for the development of antioxidant systems suitable for SBR latices.

Table 26 - Recommended starting levels for SBR formulations

'Topanol' CA	0.05 to 0.15%	
'Topanol' CA		0.05 to 0.1%
with DTDTDP		0.1 to 0.3%

Discolouring

Figures 2 and 3 show the yellowing of SBR latices with different solids contents aged up to 96 hours at 135°C.They illustrate the efficacy of 'Topanol' CA, particularly when DTDTDP is incorporated.

Figure 2 - Colour development in an SBR latex containing 76%solids (15 mil films)

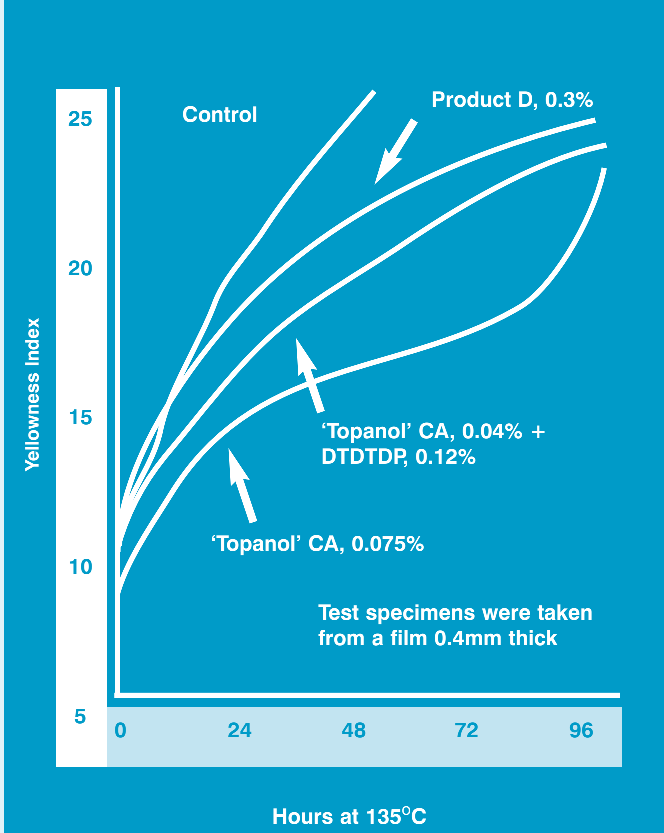
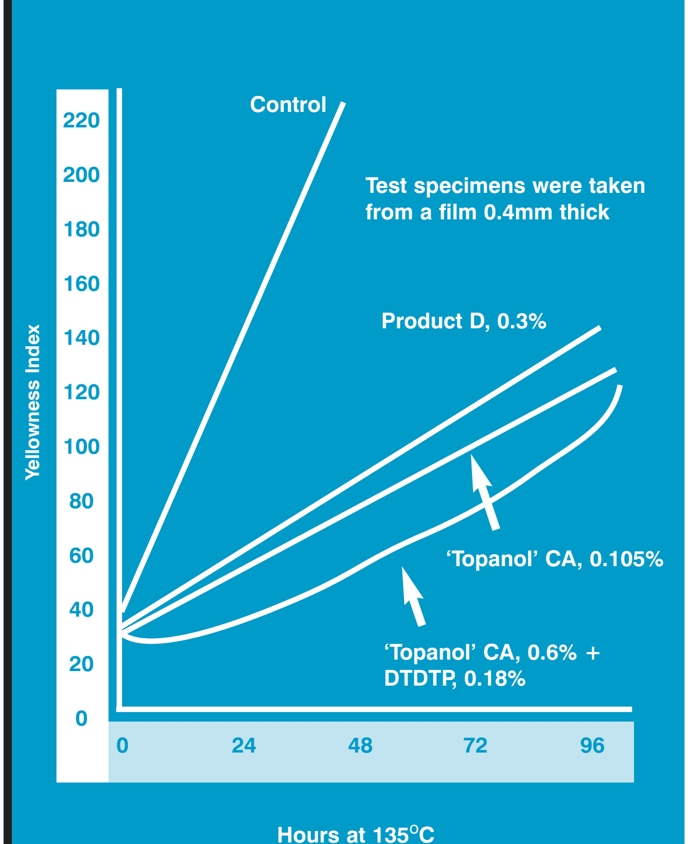


Figure 3 - Colour development in an SBR latex containing 50%solids (15 mil films)



Plasticisers for Polyvinyl Chloride (PPVC)

When added to plasticisers, 'Topanol' CA inhibits oxidative degradation and embrittlement of PVC insulation for wires and cables. PVC formulations for such applications usually incorporate plasticisers based on branched-chain alcohols and must meet specifications for minimum values of physical properties and for retention of those properties during oven-ageing for a week at a given temperature. The plasticisers are highly susceptible to thermal oxidation during coating operations and, subsequently, during the use of the products. Oxidation of the plasticiser leads to its loss by volatilisation and hence to embrittlement of the insulation.

Solubility in plasticisers

'Topanol' CA is easily dissolved in plasticisers and concentrated solutions (up to 20 to 30%) in plasticisers can be prepared for easy addition to commercial formulations. Table 27 shows the results of solubility tests carried out by observing samples stirred in an oven at 70^{o}C, noting the time required to give a clear solution. The time required for 'Topanol' CA to dissolve is typically about 30% of that required for comparable effect loadings of BPA.

Table 27 - The time required to dissolve antioxidants in two

Antioxidant	Time (minutes) to dissolve the antioxidant in the given plasticisers at 70^{o}C	
	Ditridecyl phthalate	Trioctyl trimellitate
Bisphenol A, 0.5%	125	120
'Topanol' CA, 0.05%	43	41
'Topanol' CA, 0.1%	44	42

Process stability

When PVC is aged on a Brabender Plastograph there is a gradual increase in torque to a maximum value, followed by a rapid decrease. The PVC becomes severely discoloured at about the time of peak torque. Hence the time to reach peak torque is a useful measure of the thermal stability of the composition. Table 28 gives the measurements of time to peak torque for a typical formulation in which only the type and proportion of antioxidant were varied. The results indicate that 'Topanol' CA produces a more stable compound than the other antioxidants that were investigated. Other studies have shown that usage levels of 'Topanol' CA as low as 0.02 to 0.05% on plasticiser will stabilise it effectively against oxidation through normal processing cycles.

Table 28 - The effect of antioxidants in a typical PVC formulation on time to reach peak torque(I)

Antioxidant	Time (minutes) to reach peak torque for the given antioxidant content (%) of plasticiser (DIDP)		
	0.0	0.1	0.42
BHT	68	90	108
Bisphenol A	68	95	115
'Topanol' CA	68	106	143

(I) Measured on a Brabender Plastograph at a constant jacket temperature of 200°C

Figure 4 - The effect of 'Topanol' CA on the weight loss from plasticised PVC sheet

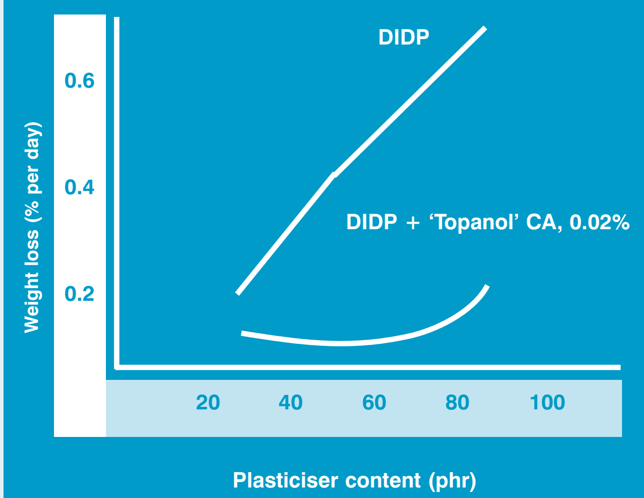
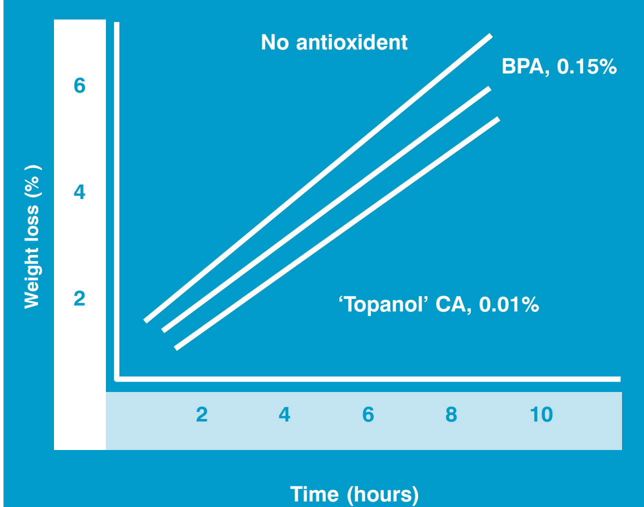


Figure 5 - The effect of antioxidant systems on the weight loss of a C7 - C11 linear phthalate at 200°C



Plasticiser volatility

The use of 'Topanol' CA substantially reduces plasticiser volatilisation. Figure 4 indicates the improvement in performance of a sheet made from plasticised PVC when a small quantity of 'Topanol' CA (0.02%) was added to the di-isodecyl phthalate used as a plasticiser. Fig 5 illustrates the results of a different test used to determine the volatilisation losses from a C7 - C11 linear phthalate heated to 200°C in an open beaker placed in a forced-draught oven. Figure 4 and Figure 5 show that the use of 'Topanol'CA reduced the losses of plasticiser, caused by its volatility very substantially and that at an additive level of 0.01% was more effective than Bisphenol A (BPA) at a level of 0.15%.

Life stability

'Topanol' CA shows significant enhancement of the tensile properties of plasticised PVC when samples are subjected to extended oven ageing tests. In formulations intended for cable insulation and sheathing, i.e. for high temperature applications, 'Topanol' CA is particularly suitable. Tables 29 and 30 illustrate the performance of formulations intended for such applications and aged for 7 days at 121°C and 136°C respectively.

Table 29 - The effects of oven-ageing (7 days at 121°C) on PVC formulations(m) containing 'Topanol' CA

Plasticiser	Antioxidant and its concentration in the plasticiser	Retention of mechanical properties (%)		Volume resistivity (Ωm x 10^{11})	
		Tensile strength	Elongation	Before ageing	After ageing
TOTM	BPA, 0.5%	91	101	5.1	12.5
	'Topanol' CA, 0.05%	95	100	3.8	9.2
	None	86	93	4.2	4.9
TOTM + DIDP	BPA, 0.4%	99	91	7.1	11.8
	'Topanol' CA, 0.04%	97	97	5.5	10.3
	None	42	34	5.0	1.1
DIDP	BPA, 0.3%	111	91	5.5	13.9
	'Topanol' CA, 0.03%	110	90	6.2	21.3
	'Topanol' CA, 0.1%	98	89	-	-
	BHT, 0.1%	69	40	-	-
	None	83	30	8.9	-
DIDP + DTDP	BPA, 0.4%	103	91	5.5	13.9
	'Topanol' CA, 0.04%	105	90	6.2	21.3
	None	(n)	(n)	4.4	(n)
DTDP	BPA, 0.5%	95	98	1.6	1.3
	'Topanol' CA, 0.05%	94	94	3.9	2.4
	None	104	89	3.7	5.7

(m) The plasticiser content of the formulations is approximately 50 parts per hundred of resin. They are suitable as insulation for "90°C wire"

(n) Embrittled by the oven-ageing

Table 30 - The effects of oven-ageing (7 days at 136°C) on PVC formulations(o) containing 'Topanol' CA

Plasticiser	Antioxidant and its concentration in the plasticiser	Retention of mechanical properties (%)		Volume resistivity ($\Omega m \times 10^{11}$)	
		Tensile strength	Elongation	Before ageing	After ageing
TOTM	BPA, 0.5%	90	81	23.0	15.3
	'Topanol' CA, 0.05%	99	108	6.3	25.9
	None	92	97	5.9	12.2
TIOTM	BPA, 0.4%	95	93	18.1	13.4
	'Topanol' CA, 0.05%	101	99	5.9	19.0
	None	73	30	4.8	6.9
DTDP	BPA, 0.3%	100	88	8.2	4.6
	'Topanol' CA, 0.05%	108	92	9.0	5.5
	None	(p)	(p)	6.0	(p)

(o) The plasticiser content of the formulations is approximately 58 parts per hundred of resin. They are suitable as insulation for "105°C wire"

(p) Embrittled by the oven-ageing

The VDE 0271 test is another technique used to assess thermal stability and has been used to provide the figures quoted in Table 31 and the curves illustrated in Figure 6. The test samples were made to Formulation F97-1-1, using DOP and DIOP as alternative plasticisers. The antioxidant was incorporated in the plasticiser. Low levels of 'Topanol' CA, 0.02 to 0.03%, provide a major contribution to stability.

Formulation F97-1-1

Component (phr)(q)	**Content**
'Corvic C®'* 65/02	100
Plasticiser	50
TBLS	6
Calcium stearate	1

(q) Parts per hundred parts of resin

*Corvic® is a registered trademark of Jiangsu Sanmu Group Corporation.

Table 31 - VDE stabilities of plasticised PVCs containing 'Topanol' CA and Bisphenol A

Plasticiser	Antioxidant and its concentration in the plasticiser	VDE (minutes) at 200°C
DOP	None	60
	BPA, 0.5%	135
	'Topanol' CA, 0.06%	135
DIOP	None	12
	BPA, 0.5%	121
	'Topanol' CA, 0.04%	121

In summary, the addition of 'Topanol' CA to PVC plasticisers gives excellent retention of mechanical and electrical properties. It is especially useful in higher molecular weight phthalates and trimellitates required for high temperature applications.

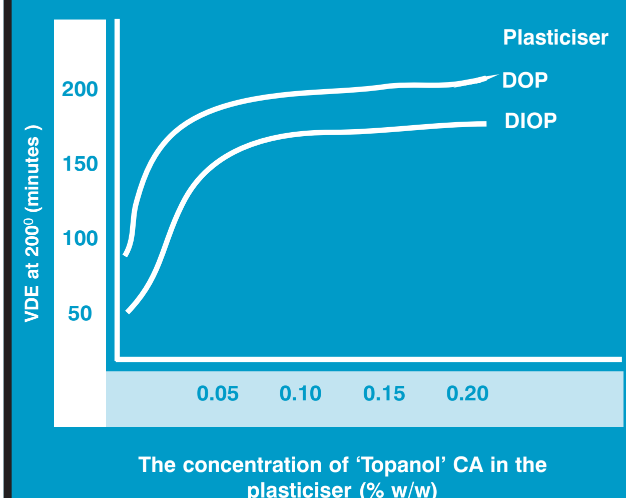
Recommended starting formulations

It is recommended that 'Topanol' CA be evaluated in the grade of PVC for which it is intended. Laboratory and manufacturing experience suggests that the formulations indicated in Table 32 will provide good starting points for the development of suitable formulations.

Table 32 - Recommended starting formulations

Type of application	Recommended antioxidant loading as a proportion of plasticiser (% w/w)
General	'Topanol' CA, 0.05 to 0.1
Prolonged service at elevated temperatures	'Topanol' CA, 0.1 to 0.3

Figure 6 - The effect of the concentration of 'Topanol' CA in plasticisers on the VDE of plasticised PVC



Automotive Applications

Where a low volatility formulation is required eg. to prevent 'fogging' of car wind shields, the use of 'Topanol' CA-SF is strongly recommended.

Polyamides

'Topanol' CA is used in the production of Nylon 66. It is introduced as an aqueous dispersion at the autoclave stage. In early work the level used was 0.5% but this is now considered to be too high. A level more suitable for starting development work is probably 0.2%. A phosphite synergist will be beneficial, used in the ratio of:

'Topanol' CA, 1 : phosphite, 3

TNPP may be suitable in some cases but where resistance to hydrolysis of the phosphite is required, more suitable phosphites such as Products G, N, Q or R, or their equivalents, may be used.

Polyamide inks

Oxidative degradation of polyamide-based printing inks results in:

- blocking of printed plastic sheets or reels
- reduced adhesion of ink to film
- development of an unpleasant odour

The benefits of 'Topanol' CA in such inks are illustrated in Tables 33 and 34.

Table 33 - The effects of 'Topanol' CA on the blocking resistance of a polyamide ink(r)

Antioxidant	Performance
None	blocking
'Topanol' CA, 0.1%	no blocking
'Topanol' CA, 0.5%	no blocking

(r) The basic formulation was:
Polyamide resin, 2: calcium rubine toner, 1

Table 34 - The storage and adhesion properties of a copper ink chip formulation(s)

Properties after storing the chips at ambient temperatures for 4 months	Antioxidant None	Antioxidant 'Topanol' CA (0.5%)
Properties of the ink chip (After 6 months storage the difference were even more marked)	pronounced odour	slight odour
	slight tackiness	tack free
Properties of an ink film Adhesion: stripping with an adhesive tape	extensive stripping	no stripping
Resistance to water wrinkling	some detachment	little detachment
Oil resistance: film detachment after rubbing	some detachment	less detachment

(s) The basic formulation was:
polyamide resin, 2 : copper phthalocyanine toner, 1

Recommended starting formulations

It is recommended that formulation development programmes are based on low levels of addition of 'Topanol' CA. An antioxidant level of 0.1% w/w of resin will be appropriate.

Hot-melt adhesives

Hot-melt adhesives are solid thermoplastic compositions of elastomers, tackifiers and stabilisers and may also contain fillers and/or plasticisers. Typical elastomers are:

- styrene-isoprene-styrene (SIS)
- styrene-butadiene-styrene (SBS)

The adhesives may be applied by melting them in, and subsequently extruding them from, a specially designed gun; or as coatings on 'Melinex*' film, heated briefly in situ. In both cases the bond created on cooling is an adhesive bond, not a chemical bond.

Stability during the heating and cooling process is an essential feature of successful formulations. In either case there may be a significant residence time at a high temperature and stability is then a particularly important feature. 'Topanol' CA is an effective stabiliser. It minimises changes in colour and viscosity, skin formation and losses in physical properties. Its effectiveness is increased when it is used with a suitable synergist such as DLTDP The test results quoted in Tables 35 and 36 were obtained by ageing for 24 hours at 160°C (to simulate conditions in the reservoir of a coating machine or an application gun) and for 10 or 20 days at 60°C (to represent extended use at temperatures higher than ambient and to accelerate effects that might be expected at ambient temperatures).

The tables show that the addition of 'Topanol' CA prevents skinning at 160°C and helps the adhesive to retain its initial viscosity. It also ensures that the adhesive systems retain their mechanical properties at 60°C.

Recommended starting formulations

Laboratory and manufacturing experience suggests that a good starting point for development work in formulations for hot melt adhesive systems will be:
'Topanol' CA, 0.4phr + DLTDP, 1.6phr

*Melinex® is a registered trademark of DuPont Teijin Films.

Table 35 - The effects of 'Topanol' CA on the ageing of hot-melt adhesives(t) at 160^{O}C

Antioxidant system	Characteristic measured	Ageing time (hours)			
		0	1	6	24
None	Viscosity (103mPa•s)	157	157	157	157
	Gardner colour	6	7	8(u)	9(u)
BHT (2 phr)	Viscosity (103mPa•s)	154	142	145	150
	Gardner colour	6	6	8(u)	10(u)
Product C + DLTDP 1 : 4 ratio (2 phr)	Viscosity (103mPa•s)	158	126	120	120
	Gardner colour	7	8	11	11
'Topanol' CA + DLTDP 1 : 4 ratio (2 phr)	Viscosity (103mPa•s)	150	150	140	140
	Gardner colour	7	7	9	11

(t) Based on tackifier and SIS at a ratio of 1 : 1
(u) Indicates skinning on the sample

Table 36 - The stability of hot-melt, pressure-sensitive adhesive films aged at 60^{O}C

Antioxidant system	Parameter measured	Antioxidant system (2 phr)					
		None		BHT		'Topanol' CA + DLTDP (1:4)	
		Before	After	Before	After	Before	After
Tackifier and SIS 1 : 1 ratio (20 day test)	Peel stick (g/cm)	790	190	1060	470	910	730
	Quick stick (g/cm)	940	350	940	350	830	830
	Failure temperature in shear (^{O}C)	95	30	92	34	83	67
Tackifier and SBS 1 : 1 ratio (10 day test)	Peel stick (g/cm)	984	160	-	-	870	410
	Quick stick (g/cm)	830	60	-	-	750	470
	Failure temperature in shear (^{O}C)	77	30	-	-	81	36

Appendix

Descriptions of materials and commercial products to which reference is made

Thioesters

DLTDP	Dilauryl thiodipropionat
DSTDP	Distearyl thiodipropionate
DTDTDP	Ditridecyl thiodipropionate
Product F	Pentaerythritoltetrakis (3-dodecyl-thiopropionate) [Seenox 412 S (Argus/Sun*)]

Phosphites

TNPP	Trisnonylphenyl phosphite
Product G	Di (2, 4-diterbutylphenyl) pentaerythritol diphosphite [Ultranox 626* (Chemtura)]
Product N	Weston 618* (Chemtura)
Product Q	Irgafos 168* (Ciba)
Product R	P-EPQ* (Ciba)

Plasticisers

DIDP	Di-isodecyl phthalate
TOTM	Trioctyl trimellitate
DTDP	Ditridecyl phthalate
TIOTM	Tri-isooctyl trimellitate
DOP	Dioctyl phthalate
DIOP	Diiso-octyl phthalate

Materials

Product A	Octadecyl 3-(3,5-di-t-butyl-4-hydroxy phenyl) propionate [Irganox 1076* (Ciba)]
Product B	4,4'-Thiobis (6-tert-butyl-3-methyl phenol) [Santonox®* (Tetrahedron)]
Product C	2,2 methylene-bis- (6-1 methylcyclo-hexyl)-p-cresol [Lowinox WSP* (Addivant)]
Product D	A butylated reaction product of p-cresol and dicyclopentadiene
Product E	2,2'-Ethylenebis (4,6-di-tertiary-butylphenol)
Product H	Tetrakis (methylene-3,(3,5-diterbutyl-4-hydroxyphenyl)propionate)methane [Irganox 1010* (Ciba)]
Product I	1,3,5-Trimethyl-2,4,6-tris (3,5-di-t-butyl-4-hydroxybenzyl) benzene
Product J	1,3,5-Tris(4-t-butyl-3 hydroxy-2,6 dimethyl-benzyl) 1,3,5-triazine-2,4,6-(1H,3H,5H) trione
Product K	Epon 1002* (Momentive)
Product L	Vanox 3240* (Vanderbilt)
Product M	Vanox 3250* (Vanderbilt)
Product O	Cyasorb 531* (Cytec)
Product P	Tinuvin 770* (Ciba)
Product S	1,2-Bis(3-(3,5-ditert-butyl-4-hydroxyphenyl) propionic acid) hydrazide [Irganox MD 1024* (Ciba)]
Product T	Wingstay L* (Goodyear)
Product U	Wingstay SN-1* (Goodyear)
BHT	2,6-Di-tertiarybutyl-4-methyl phenol
BPA	Bisphenol A
HALS	Hindered amine light stabiliser
OABH	Oxalic acid-bis(benzylidene hydrazide)
SBS	Styrene-butadiene-styrene
SIS	Styrene-isoprene-styrene
TBLS	Tribasic lead sulphate

Health and safety

Health and handling advice on the 'Topanol' CA range is given in an individual product safety data sheet, available on request.

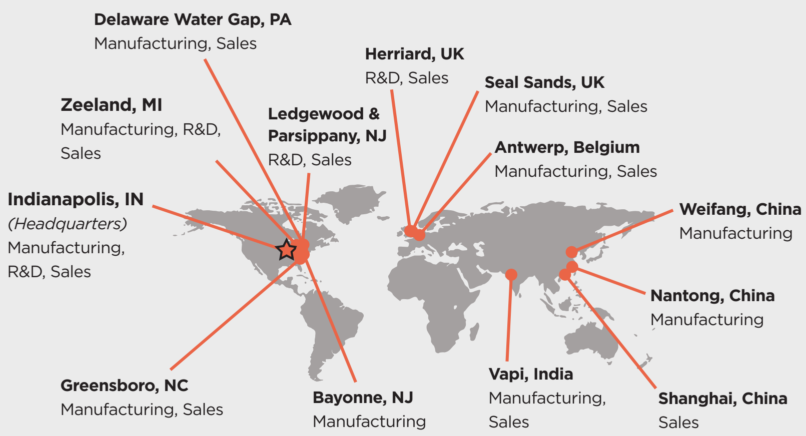
Technical service and applications advice

Please contact Vertellus Specialties Inc. for advice on the use of 'Topanol' CA range of products. We will be pleased to discuss your requirements and provide technical support. Samples of all products are available on request. Our standard sample size is 200g.

Acknowledgement

'Topanol' is a registered trademark, the property of ICI PLC and is used under licence by Vertellus Specialties Inc.

Global Footprint



Global Sales Offices, Manufacturing Facilities & Distributor Network

Vertellus is a leading provider in the world of specialty chemicals for agriculture, nutrition, pharmaceutical, medical, personal care, plastics, coatings and industrial markets.

- 500+ products, notably the world's first producer of pyridine
- 150+ years of experience in the development of specialty chemicals
- 13 manufacturing plants on three continents

Besides being a global leader in the manufacture of picoline and pyridine products, we are also a leading producer of cyanopyridine, and nicotinic acid/amide.

We're recognized as the leading innovator in natural-based castor oil chemistry and citrate esters, providing performance solutions for a wide range of demanding applications for an ever-changing marketplace.

From crop protective chemicals to the highest standards of production for FDA-approved pharmaceutical applications, Vertellus consistently meets the challenge.

Vertellus®

CORPORATE OFFICE

Vertellus Specialties Inc.
201 N. Illinois Street, Suite 1800
Indianapolis IN 46204 USA
Phone: 317-247-8141
Fax: 317-248-6472

www.vertellus.com

AGRICULTURE | NUTRITION | PHARMACEUTICAL | PERSONAL & CONSUMER CARE | PLASTICS & POLYMERS | C.A.S.E. | INDUSTRIAL SPECIALTIES