

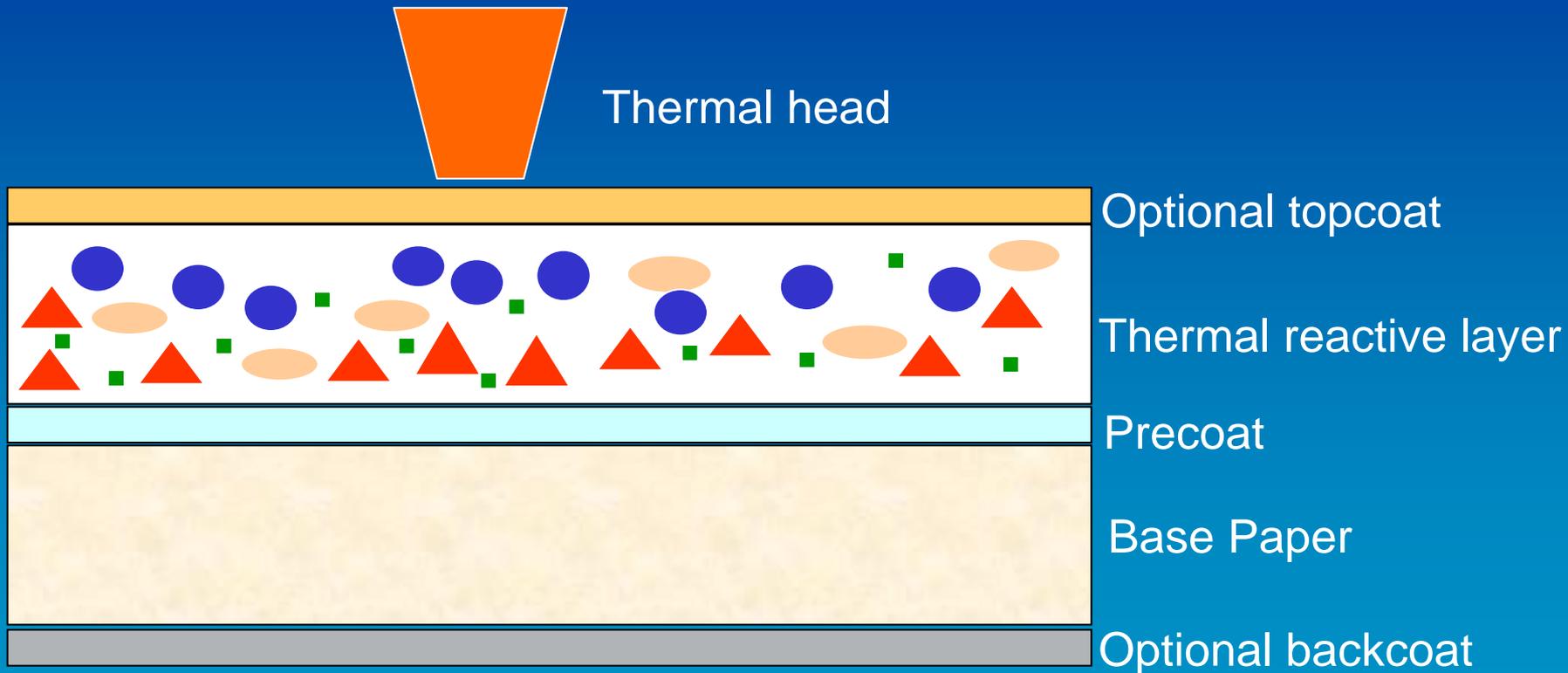


BPA as a Developer in Thermal Paper and Alternatives

Identifying Alternative Developers

July 15, 2010

Cross section of thermal paper

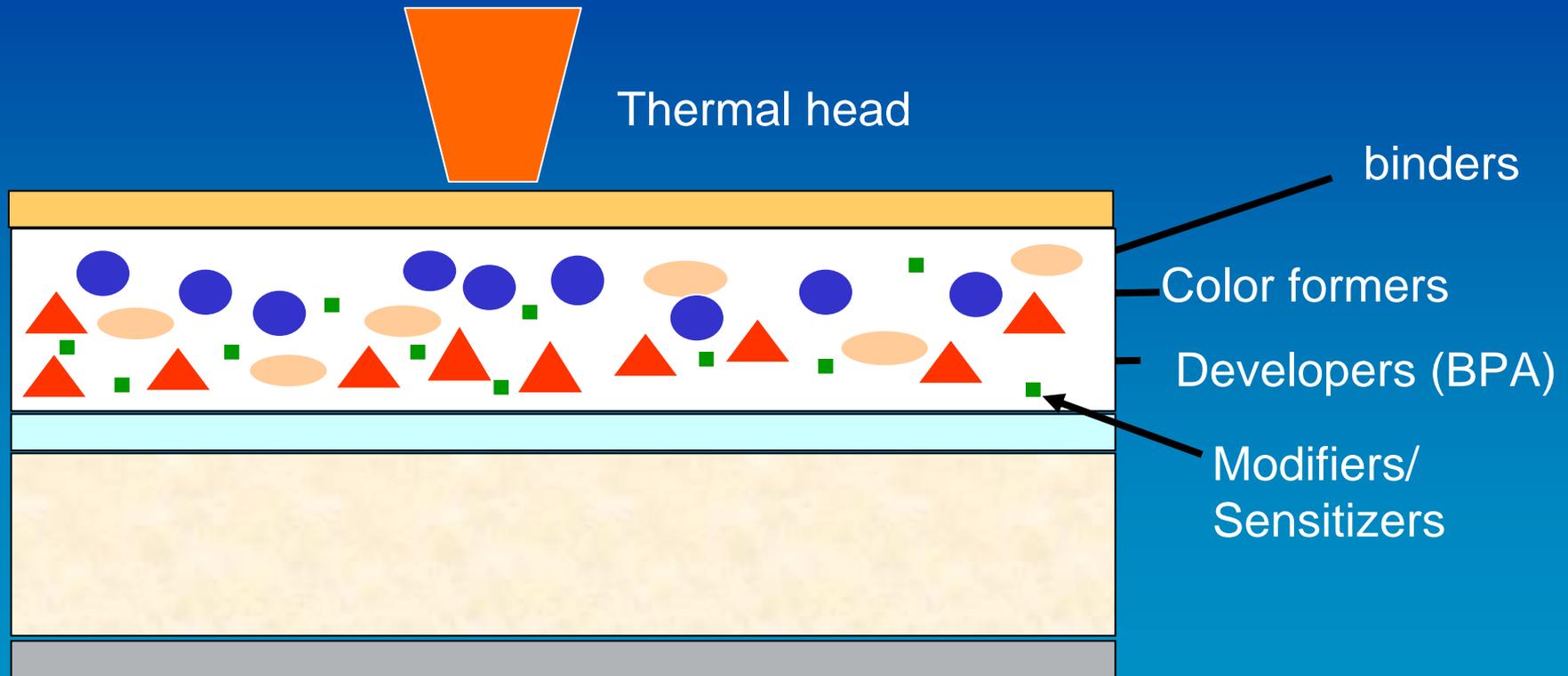


Based on Koehler Product Brochure

Components of thermal paper

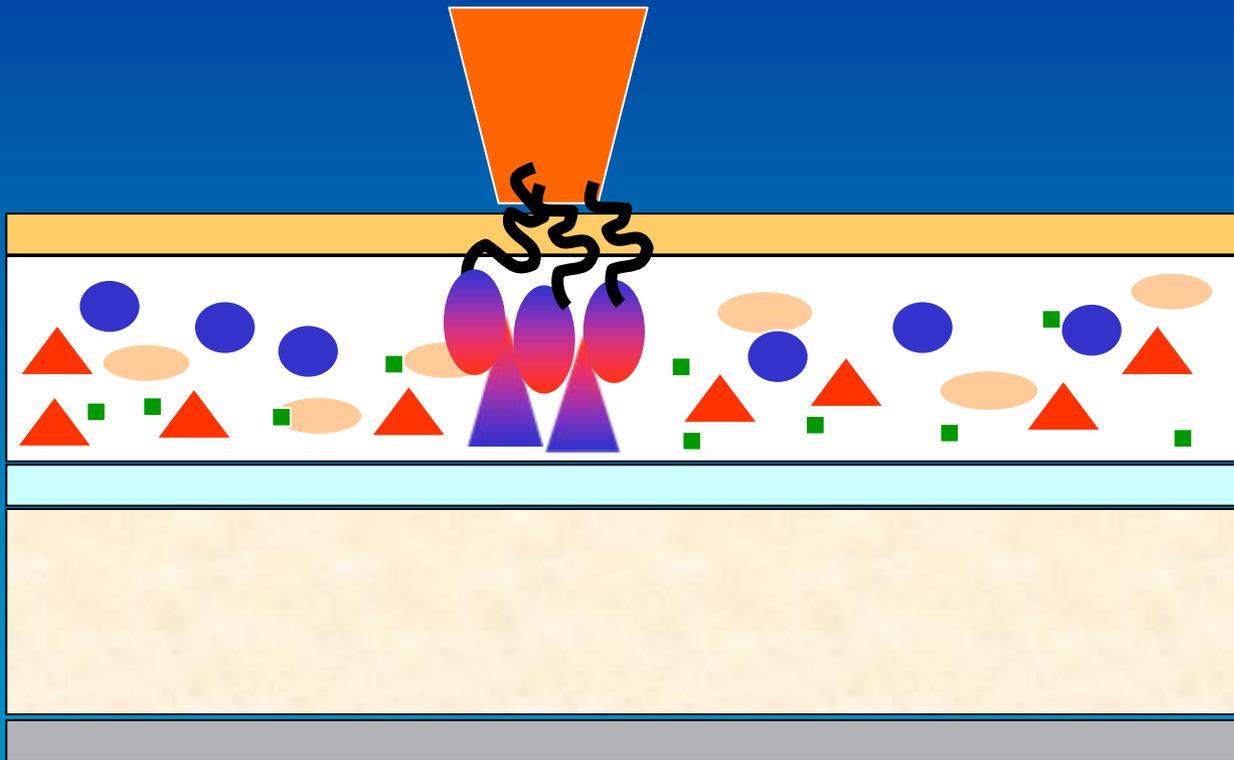
- Color former – Leuco dye that is light/colored or colorless but will change to a dark color with the addition of a proton which opens the lactone ring.
- Color developer – the weak acid that donates a proton to the color former, changing it from light to dark.
- Modifier/sensitizer – can reduce the melting point of the color former & developer mix.
- Binders –adhere the coating to the paper.

Cross section of thermal paper



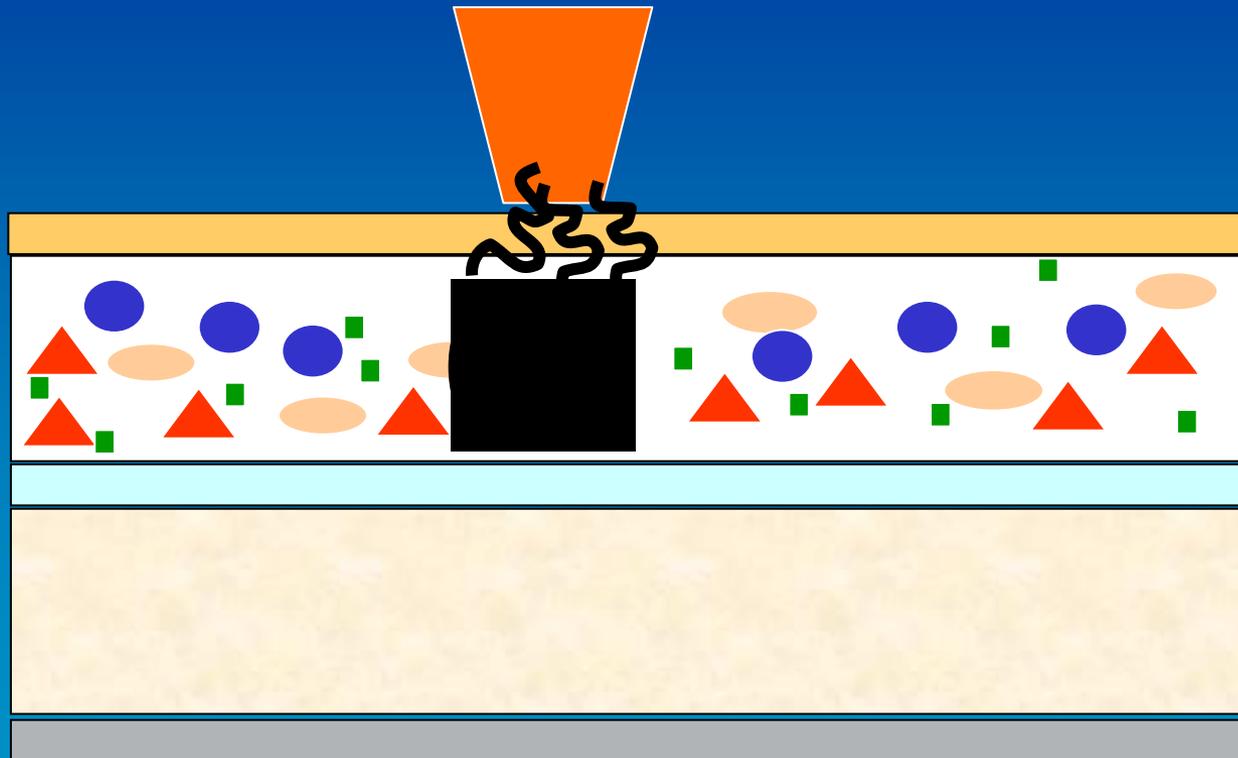
Based on Koehler Product Brochure

Developer and color former react when heated



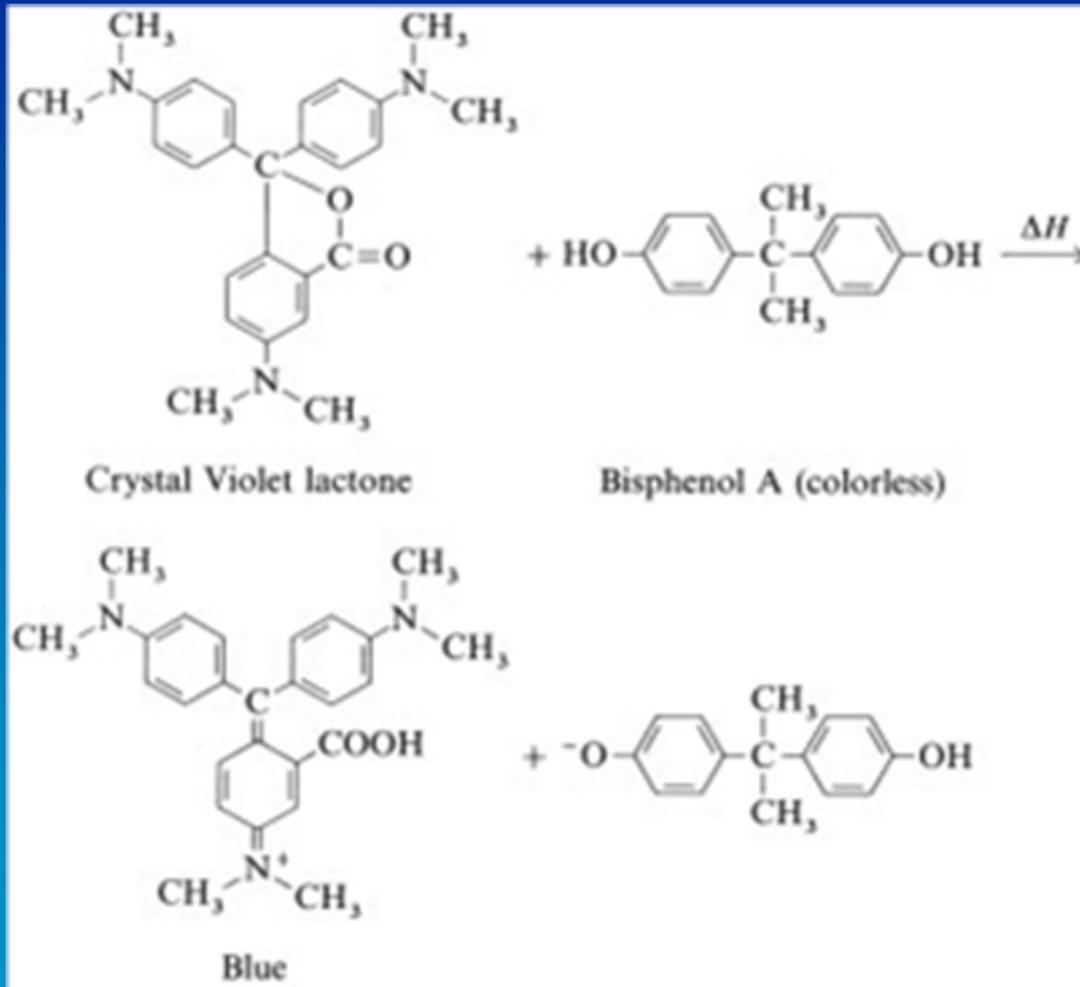
Based on Koehler Product Brochure

Color former turns dark



Based on Koehler Product Brochure

Example of the color-forming reaction



Required properties of developers

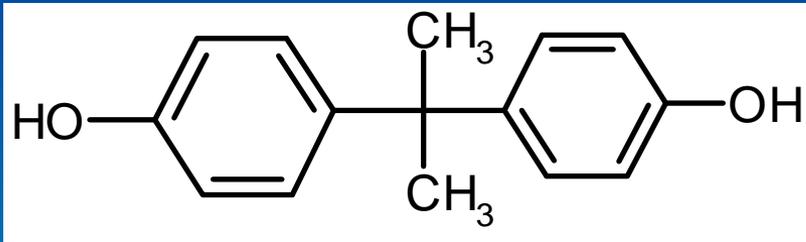
- pKa range or acidity
- Solubility
- Melting point
- Others?

Characteristics of an effective developer

- Low/no background imaging (specific).
- Fully react with the color former when heated by the thermal head (sensitive).
- React at the temperatures of the specific printer.
- Stable
- Appropriate permanence for the application.
- Impart the appropriate performance/cost balance.
- Be feasible for large scale production.
- Others?

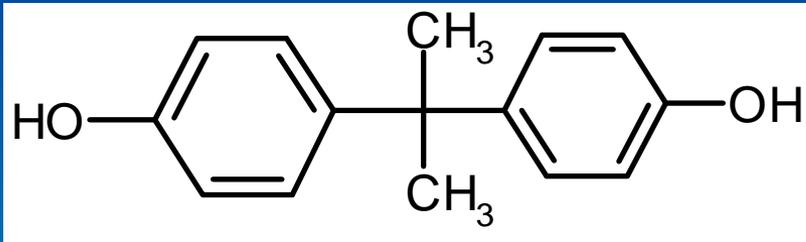
Bisphenols

BPA 80-05-7

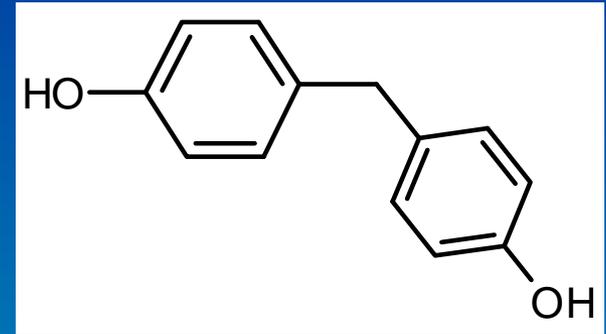


Bisphenols

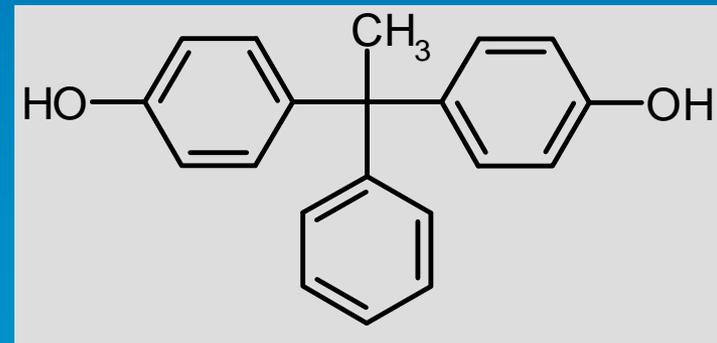
BPA 80-05-7



Bisphenol F 620-92-8

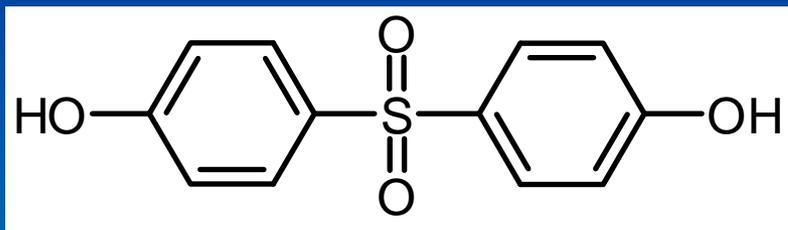


Bisphenol AP 1571-75-1

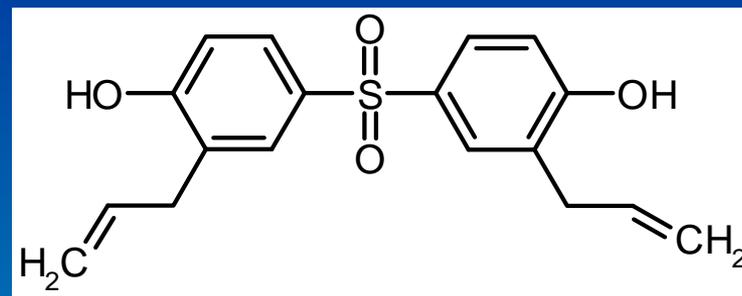


Sulfones

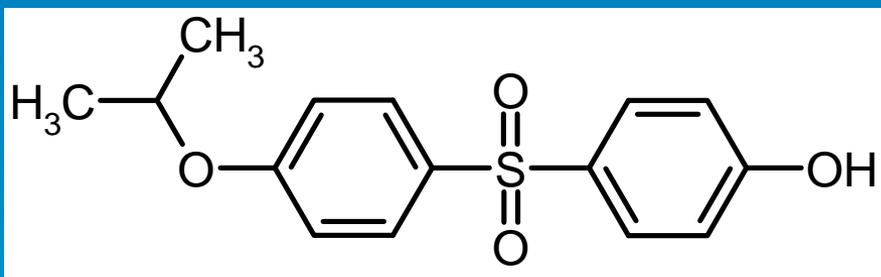
Bisphenol S 80-09-1



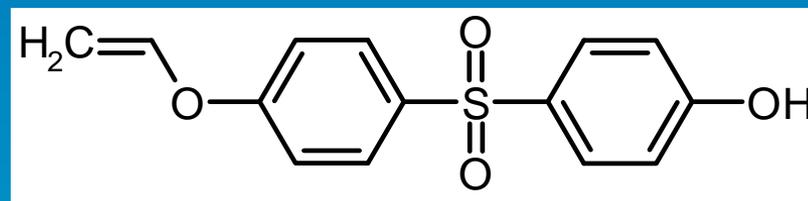
bis-(3-allyl-4-hydroxyphenyl) sulfone
41481-66-7, TGSA



4-Hydroxy-4'-isopropoxydiphenylsulfone
D-8 95235-30-6

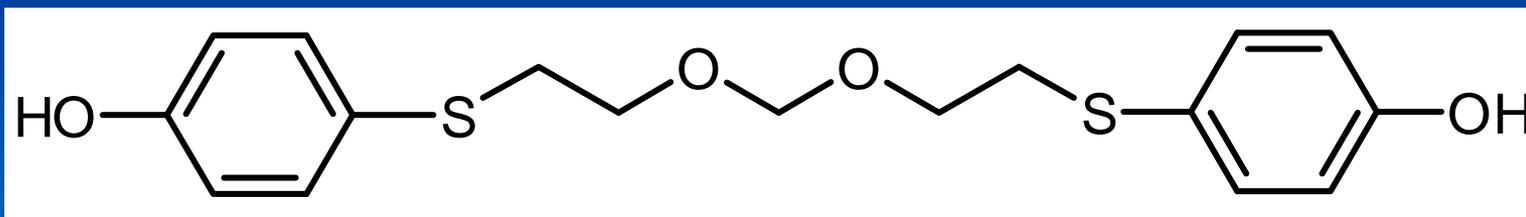


Phenol,4-[[4-(2-propen-1-yloxy)phenyl]sulfonyl]-
BPS-MAE 97042-18-7

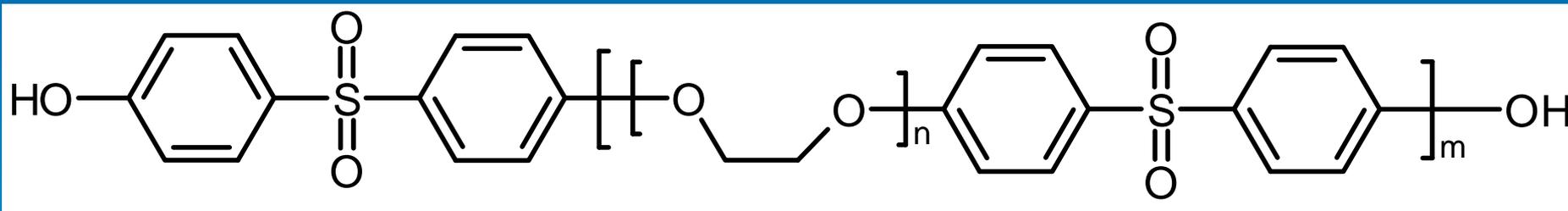


Other Phenols

1,7-bis(4-hydroxyphenylthio)-3,5-dioxahexane

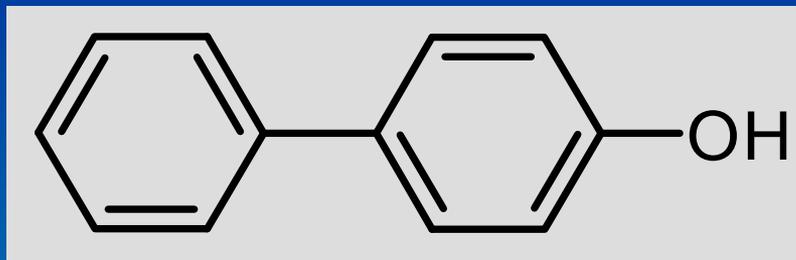


Phenol, 4,4'-sulfonylbis-, polymer with 1,1'-oxybis[2-chloroethane] 191680-83-8, D-90

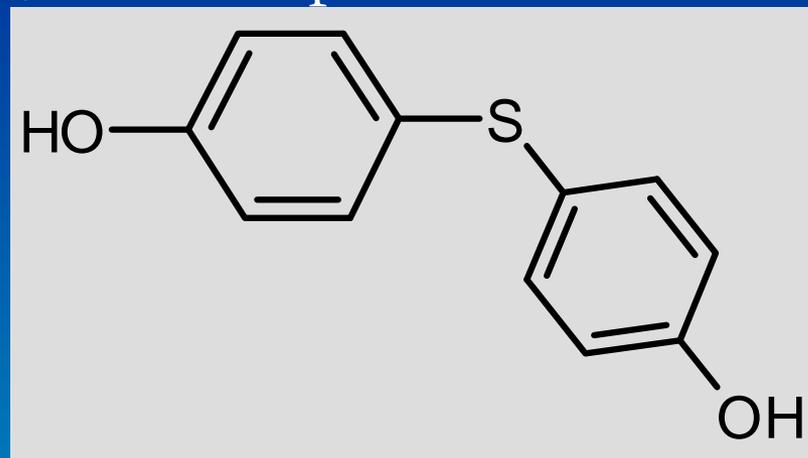


Other Phenols - less likely to be feasible

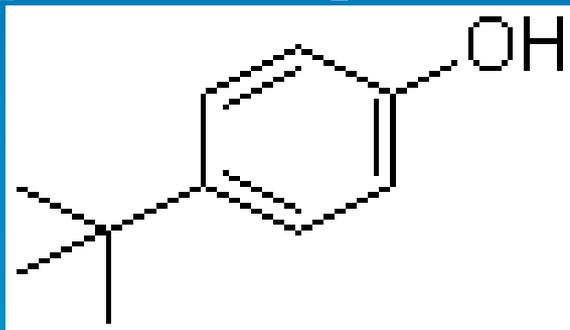
p-Phenylphenol 92-69-3



4,4'-thiobisphenol 2664-63-3



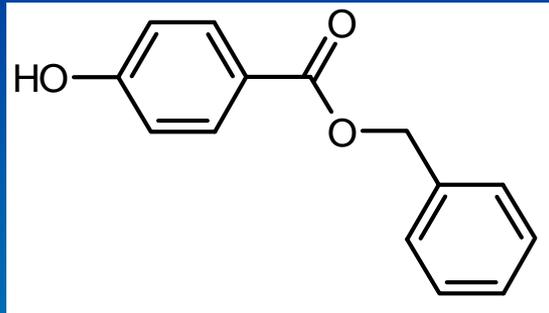
p-tert-butylphenol 98-54-4



Phenolic Esters - less likely to be feasible

Benzyl 4-hydroxy-benzoate

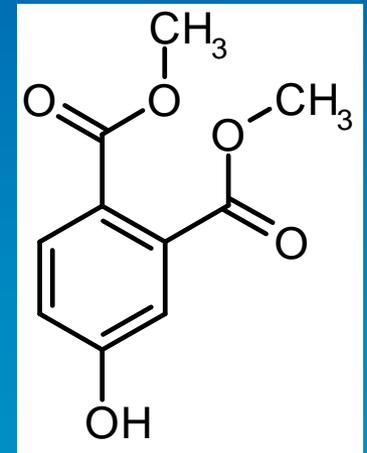
94-18-8



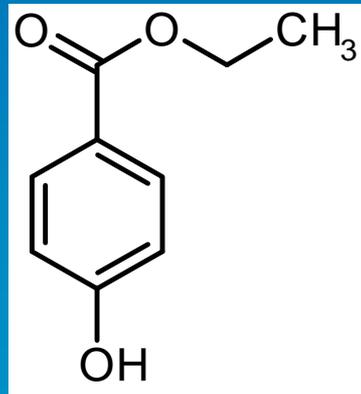
Dimethyl-4-hydroxyphthalate

22479-95-4

DMP-OH

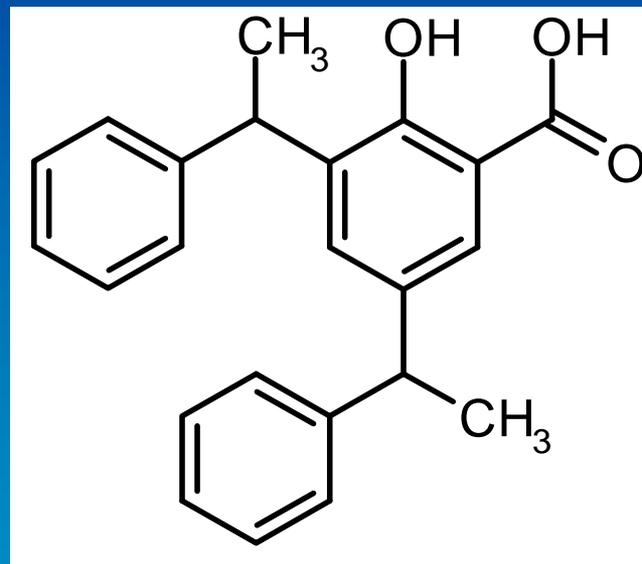
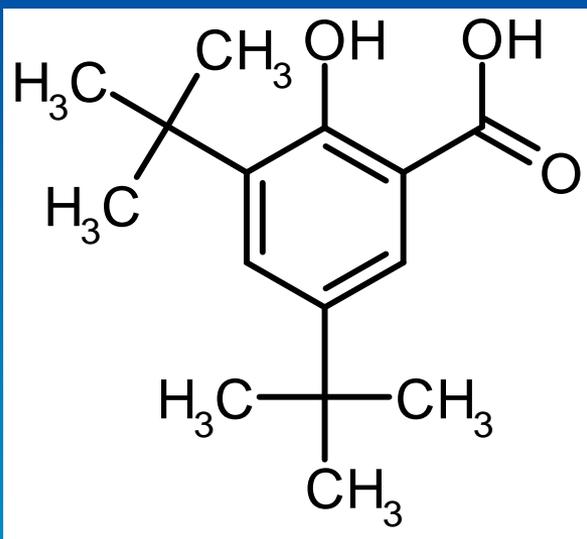


Ethylparaben 120-47-8



Salicylic acids - less likely to be feasible

- 3,5-di-tert-butylsalicylic acid (CASRN 19715-19-6)
- 3,5-di- α -methylbenzylsalicylic acid



Alternative Developers

- Palygorskite or attapulgite
 - Hallosyte
 - Kaolin and colloidal silica
 - Phenolic novolak resins
-
- **Partner Nominated**

Winnowing Criteria?

- Drop in replacement
- Considered likely to be functional
- Manufacturer willing to demonstrate proof-of-concept.

Discussion topics

- Other physical properties of developers?
- Other characteristics of an effective developer?
- Chemicals to cross off our list?
- Chemicals to add to the list?

Exposure to BPA

- 93% of Americans have measurable levels of BPA in their urine.¹
- 2.58 ug/g of creatinine - normalized average concentration.¹
 - 95th percentile – 11.2 ug/g¹
 - Kids 6-11 yrs had the highest concentration – average 4.58ug/g.¹
 - Recent study suggests non-dietary exposure to BPA may be more significant than previously recognized.²

1. Centers for Disease Control and Prevention. *Fourth National Report on Human Exposure to Environmental Chemicals*. <http://www.cdc.gov/exposurereport/>. December 2009.
2. Stahlhut, et. al. 2009. Bisphenol A data in NHANES suggest longer than expected half-life, substantial nonfood exposure or both. *Environmental Health Perspectives*.

BPA levels in media

- Surface water - median concentration of 0.14 $\mu\text{g}/\text{L}$ and a maximum concentration of 12 $\mu\text{g}/\text{L}$ in 41.2% of 85 samples collected from U.S. streams in 1999 and 2000 The maximum concentration of 12 $\mu\text{g}/\text{L}$ is an outlier .
- one U.S. study reported maximum BPA concentrations of 1.7 $\mu\text{g}/\text{L}$ in landfill leachate (Crain et al., 2007).
- Landfill leachate from other countries contained more than 500 $\mu\text{g}/\text{L}$ of BPA (Crain et al., 2007).
- Klecka et al. (2009) reported a median concentration of 0.6 ppb BPA in North American freshwater sediments, including nondetected samples; BPA concentrations in samples from the United States ranged from 1.4 to 140 ppb dry weight
- 0.01 parts per million (ppm) to 50 ppm in marine sand – PRELIMINARY STUDY (<http://www.grist.org/article/new-evidence-that-bpa-has-widely-contaminated-the-oceans/>)

1. Kolpin et al., 2002.
2. Crain et al., 2007.
3. Klecka et al. 2009

BPA levels in media

- Level in receipts – $0.6\text{mg}/\text{in}^2 \sim 6 \text{ mg}/\text{receipt}^1$
 - Estimate 6 ppm/receipt
- Dust – detectable in 25% of samples²
 - Levels up to 700 ng/g dust (range 35-700ng/g)
 - Unclear how much paper contributes to BPA in dust
- Indoor air - detectable in 50% of samples²
 - Up to 193 ng/m³ (range 1.8 – 193)
- Levels in food²
 - 1.49ng/g – 192 ng/g (0.192 ppm)

1. John Warner, personal communication.

2. Wilson, et al. 2007 An observational study of the potential exposures of preschool children to pentachlorophenol, bisphenol-A, and nonylphenol at home and daycare. Environmental Research.

Impact on Paper Recycling

- No published studies on BPA in US recycled paper streams
- European Union data:
 - Amount of BPA in paper sludge (used to make recycled paper) ~ 0.18 - 3.28 BPA per kg.^[i]
 - BPA in recycled paper towels ranged from 0.6 to 24.1 mg/kg paper, while BPA in virgin paper ranged from 0.03 – 0.1 mg/kg paper.^[ii]
 - BPA in toilet paper ranged from 3 – 46 mg/kg dry mass, and BPA in a variety of other waste paper ranged from 0.09 – 5.10 mg/kg dry mass^[iii].
 - BPA concentration in recycled paper was 10 or more times higher than in virgin products: 0.19 to 26 µg/g recycled paper versus 0.034 to 0.36 µg/g virgin paper.^[iv]
- High degree of variability associated with differences in processing and treatment techniques

[i] European Union. 2010. Risk Assessment Report, 4,4'-Isopropylidenediphenol (Bisphenol-A), CAS No: 80-05-7, (February 2010).

[ii] Vinggaard AM, Körner W, Lund KH, Bolz U, Petersen JH. 2000. Identification and quantification of estrogenic compounds in recycled and virgin paper for household use as determined by an in vitro yeast estrogen screen and chemical analysis. *Chem Res Toxicol.* 13(12):1214-22.

[iii] Gehring M, Vogel D, Tennhardt L, Weltin D, Bilitewski B. Undated. Bisphenol A contamination of wastepaper, ellulose and recycled paper products. <http://rcswvvr.urz.tu-dresden.de/~gehring/deutsch/de/vortr/040920ge.pdf>

[iv]. Ozaki A, Yamaguchi Y, Fujita T, Kuroda K, Endo G. 2004. Chemical analysis and genotoxicological safety assessment of paper and paperboard used for food packaging. *Food Chem Toxicol.* 42(8):1323-37.

Types of thermal printing

- Direct
 - Focus of this project
 - Dye and developer are impregnated onto the paper
- Thermal Transfer
 - Relies on a heated ribbon

Manufacturing

- Slurries are spread on paper.
- Various other coatings may be added.
- Converters cut the paper rolls to appropriate size.
- Adhesives may be added to the back for printing labels.