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Analysis of alternatives for BPA in thermal paper

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Report 1515

Colophon

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Abstract

In May 2014, France submitted a restriction proposal for bisphenol A (BPA) used in thermal paper due to a perceived risk for human health. This report is an expert opinion on the feasibility of the alternatives for BPA for application in thermal paper as listed in this restriction proposal.

Out of the seven phenolic substances listed in the French proposal only Bisphenol S and D8 can be considered as feasible alternatives since they are already applied as developer in thermal paper. However, given their high structural similarity to BPA (and estradiol), a similar endocrine disrupting potential can be expected, or is already confirmed, for these bisphenol derivatives. This makes it doubtful whether substitution by these substances will bring any benefits to public health and environment.

Out of the three non-phenolic substances listed in the French proposal, at least one, i.e. 1,2-diphenoxyethane, is not active as a dye developer in thermal paper, and based on expert opinion should be removed from the list.
The remaining two non-phenolic substances, i.e. Pergafast 201 and Urea Urethane can be considered as feasible alternatives since they are already applied as developer in thermal paper.

Furthermore, various other potential alternatives for BPA in thermal paper applications have been identified, that have not been included in public reports on alternative dye developers thus far. Gallic acid esters are biobased, commercially available, food-grade substances that are, according to the literature, known dye developers. Diphenolic acid is another example of a biobased, commercially available phenolic substance, that is promoted as alternative to BPA in various applications.

Content

1 Introduction

REACH aims to ensure a high level of protection of human health and the environment from the risks that can be posed by chemicals by means of registration, evaluation, authorisation and/or restriction of chemicals. One example of a substance potentially causing effects to human health is bisphenol A (BPA) through its use in thermal paper. In May 2014, France submitted a restriction proposal for BPA used in thermal paper due to a perceived risk for human health.[1] Besides an extensive risk assessment, the restriction proposal consists among others of an analysis of alternatives for the use of BPA as a dye developer in thermal paper.

The Risk Assessment Committee (RAC) and the Socio-Economic Analysis Committee (SEAC) of the European Chemical Agency (ECHA) are now evaluating the French restriction proposal on BPA. Both Scientific Committees will deliver their (draft) opinions on the dossier by March 2015, to serve as input for the European Commission to conclude upon the need for a European wide restriction on BPA in thermal paper. As part of the review process, the restriction proposal by France is open for Public Consultation (ends by 18 December 2014). Comments brought up in the PC will be included in the review process by RAC and SEAC.

This report aims to review the alternatives for BPA in thermal paper. The review includes an expert-view evaluation of the data on alternatives presented in the French restriction dossier. Besides that, the project aims to add further information on alternatives to BPA in this application as far as this information is available in the public domain. In this additional assessment, the focus is on potential bio-based alternatives and knowledge on alternatives available at WUR-FBR based upon hands-on experience with the development of alternatives.

Depending on the outcome of this report, the results will be used to comment on the restriction dossier in the PC.

This report includes the following tasks:

1. A review of the analysis of BPA alternatives as presented in the restriction proposal[1] above, including;
   a. The availability of the alternatives
   b. The technical feasibility of the alternatives
   c. The economic feasibility of the alternatives
2. A completeness check of the analysis of alternatives as presented in the restriction proposal. This includes a check on any information available in the public domain on chemical alternatives that are additional to those presented in the restriction proposal. Assessment is made by means of a short description and analysis (see task 1). The aim of this action is to review (potential) (bio-based) substance alternatives for the use of BPA in thermal paper.
3. A brief assessment of alternatives of BPA in other applications. The aim of this task is to check whether alternatives discussed under tasks 1 and 2 are technically feasible alternatives for other applications of BPA. This can for example be presented in a cross-table. Applications that need to be included are at least: use as a monomer for the production of polycarbonate plastics and articles thereof (food contact materials and non-food applications, including medical devices for which information is available), use as a monomer for the production of epoxy resins and articles thereof (food contact applications like can-coatings, and non-food applications like construction materials, paints, coatings).

The restriction proposal from France on BPA in thermal paper – part C, serves as the main information input for this report. Furthermore, two other recent reports on the subject matter, i.e. the 2013 Arcadis report "Inventarisation of the use of bisphenol A at the working place and investigation of the risks of BPA substitutes"[2], and the 2014 Danish Environmental Protection Agency (DEPA) report "Alternative technologies and substances to bisphenol A (BPA) in thermal paper receipts"[3] have been used as background information.

2 Results & Discussion

Background

Bisphenol A (BPA, figure 1) is an important chemical building block for the production of high performance materials like polycarbonate (for e.g. sheets for roofing and glazing, optical media, IT-parts, spectacle lenses, medical devices, leisure articles and food contact materials)[4] and epoxy resins (e.g. for coatings, adhesives and composite materials such as those using carbon fiber and fiberglass reinforcements)[4].
BPA is also an endocrine disruptor that closely mimics the structure and function of the human hormone estradiol (figure 1).[5] Since this has been shown to cause negative health effects, exposure to free BPA should be limited.

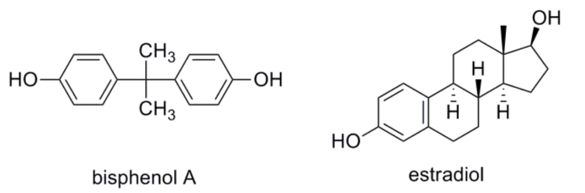


Figure 1: Chemical structures of BPA and estradiol.

BPA is used in its monomeric form as an additive (developer) in the coating of thermal paper. The major application of thermal paper is point-of-sale (POS) receipts (e.g., supermarket receipts), followed by self-adhesive labels, lottery tickets and fax paper.[2] BPA is currently the by far most used developer. The amount of BPA used in thermal paper in the EU is 1,890 tonnes per year.[2] This amount is used to make an equivalent of ca. 168,000 tonnes of paper per year. Thermal paper is basically composed of a base paper over which a thermally reactive layer is applied. This layer contains a binder, a colour-forming substance (thermochromic ink) and a colour developer. When the paper is heated above the melting point of the binder, the acidic colour developer protonates the thermochromic ink which results in a change of colour (figure 2).

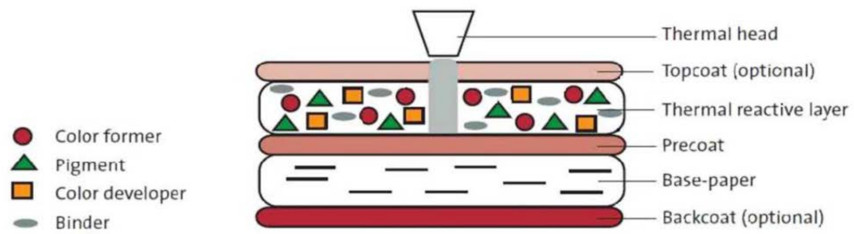


Figure 2: Schematic structure of thermal paper.[1]

Figure 3 shows an example of a thermochromic ink, also known as leuco dye. The leuco dye (usually spirolactones, fluoranes, spiropyranes, etc.) can be chemically transformed from a non-coloured to a coloured form, in this case by a pH change (a process known as halochromism).[5]

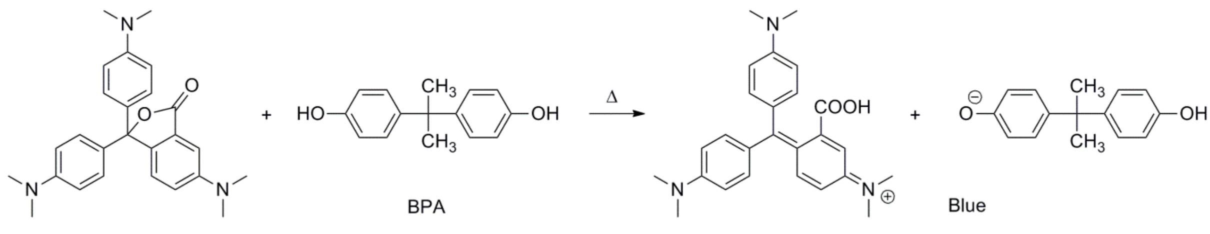


Figure 3: Example of halochromism; the transformation between leuco and colored form of crystal violet lactone.[5,6]

In thermal paper BPA acts as the weak proton donor (pKa 9.6 - 10.2)[7] required for the halochromic effect. According to a US-EPA report pKa range or acidity, melting point and solubility of BPA alternatives should be comparable with those of BPA.[6]

The French restriction proposal identifies 30 potential alternatives for BPA based on 6 prior reports. A refinement based on exclusion and inclusion criteria has subsequently resulted in a list of 10 potential realistic alternative dye developers to BPA in thermal paper. It should be mentioned here that 5 chemicals identified in a previous study[8] were not selected for further assessment based on poorer performance compared to BPA. These commercially available antioxidants are different types of so called hindered phenols. The pKa values of these phenols are higher than those of BPA, e.g. 12.6 for BHT[9], which is indicative of the importance of the acidity of BPA alternatives. Furthermore, also steric hindrance of the phenolic hydroxyl group is expected to have a negative effect on the reactivity.[10]

Task 1: Evaluation of alternatives

In the following section the ten alternative dye developers selected in the French restriction proposal are discussed according to the criteria mentioned in the introduction, these include seven phenolic and three non-phenolic substances. Each assessment is followed by a conclusion on overall feasibility based on expert opinion.

Definition of terminology
In this report different conclusions based on the expert opinion by WUR-FBR with regard to the criteria Availability, Technical feasibility, and Economic feasibility are given. The following list is a definition of the terminology used in this report.

- Confirmed: based on public information on actual production figures, prices, or actual application as dye developer in thermal paper
- Feasible: feasible according to expert opinion based on physico-chemical properties of the substance (i.e. chemical similarity to BPA), or commercial use in other applications.
- Unknown: cannot be assessed due to lack of publically available information. However, cannot be ruled out.
- None: can be ruled out based on lack of required chemical properties.

Note that the assessment of human health and environmental hazards of the alternatives is outside of the scope of the assessment presented in this report. However, for some alternatives readily available information on toxicological properties such as indications of potential endocrine disrupting properties is reported here, but these aspects were not included in the feasibility criteria as such. It is acknowledged that hazard and risk assessment do play a crucial role in various stages of the choice and development of alternatives for specific uses as the restriction on the use of BPA in thermal paper aims to reduce exposure to this chemical with an endocrine mode of action. In general, the replacement of BPA with structural analogues with a similar endocrine mode of action and potency is therefore not favourable. However, alternatives may also have other properties such as environmental toxicity or dermal sensitization. Such properties may influence the final feasibility conclusion to a large extent dependent on the results of the chemical safety assessment.

Phenolic alternatives

An overview of the chemical structures of the phenolic alternatives is given in figure 4.

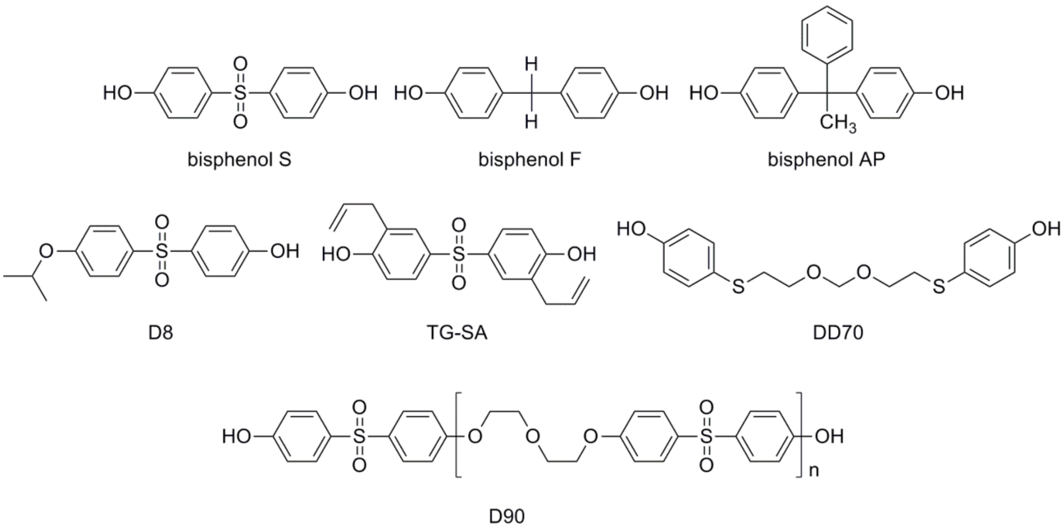


Figure 4: Overview of phenolic BPA alternatives.

Bisphenol S (BPS) [80-09-1]

- Availability: *confirmed.*

BPS is a commercial product which is marketed as BPA replacement in a variety of applications, both in monomeric form (e.g. in some forms of BPA-free thermal paper) as well as in polymers (polyether sulfones).

- Technical feasibility: *confirmed.*

BPS is already used in thermal papers, e.g. in the US and in Japan.[1]

- Economic feasibility: *confirmed.*

Thermal paper with BPS is the most common and cheapest alternative to BPA (approx. 5-10% more expensive than BPA based paper).[3]

- Conclusion based on expert opinion: BPS is a confirmed alternative.

Bisphenol F (BPF) [620-92-8]

- Availability: *unknown.*

BPF is not registered under REACH so far.[1] No data are available on tonnage produced.

- Technical feasibility: *feasible.*

Based on its structural resemblance to BPA, it is highly feasible that BPF can act as a developer in thermal paper.

- Economic feasibility: *unknown.*

No data available.

- Conclusion based on expert opinion: BPF is a potential alternative, yet more data are required.

Bisphenol AP (BPAP) [1571-75-1]

- Availability: *unknown.*

BPAP is not registered under REACH so far.[1] No data are available on tonnage produced or marketed.

- Technical feasibility: *feasible.*

Based on its structural resemblance to BPA, it is feasible that BPAP can act as a developer in thermal paper .

- Economic feasibility: *unknown.*

No data available.

- Conclusion based on expert opinion: BPAP is a potential alternative, yet more data are required.

D8 [95235-30-6]

- Availability: *confirmed.*

D8 is a commercial product. Data on tonnage of D8 produced/imported are indicated as confidential in the REACH registration dossier.[1]

- Technical feasibility: *confirmed.*

According to one thermal paper manufacturer D8 is used as an alternative to BPA in thermal paper labels.[3]

- Economic feasibility: *unknown.*

No data available.

- Conclusion based on expert opinion: D8 is a confirmed alternative.

TG-SA [41481-66-7]

- Availability: *confirmed.*

TG-SA is a commercial product.[2] Data on tonnage of TG-SA produced/imported are indicated as confidential in the registration dossier.

- Technical feasibility: *unknown.*

There are no indications about the actual use of TG-SA in thermal paper.[1] Although TG-SA has a bisphenol structure, the presence of the pendant allyl groups can have various physico-chemical effects that would preclude its use as a dye developer. Without additional data, technical feasibility cannot be properly assessed.

- Economic feasibility: *unknown.*

No data available.

- Conclusion based on expert opinion: TG-SA is a potential alternative, yet more data are required.

DD70 [93589-69-6]

- Availability: *confirmed.*

DD70 is a commercial product. Data on tonnage of DD70 produced/imported are indicated as confidential in the registration dossier. Most probable producer is Sumitomo Seika Chemicals.[11]

- Technical feasibility: *unknown.*

There are no indications about the actual use of DD70 in thermal paper.[1] However, given the apparent application of D90 in thermal paper[3], also the use of DD70 could be feasible. More data are required for a proper assessment

- Economic feasibility: *unknown.*

No data available.

- Conclusion based on expert opinion: TG-SA is a potential alternative, yet more data are required.

D90 [191680-83-8]

- Availability: *feasible.*

The data on the tonnage of D90 produced, used or placed on the EU market are not publicly available as it is claimed confidential on the registration dossier.[1]

- Technical feasibility: *unknown.*

According to the D.E.P.A. report, D90 is known to be used in thermal paper.[3] The manufacturers of thermal paper consulted by INERIS, 2013 confirmed that D90 is already used in thermal paper.[1] However, according to ETPA, as a printing stabilizer it cannot be used to reduce the amount of BPA in the paper, but only to improve the stabilization of the image, and cannot really be considered as alternatives to BPA.

- Economic feasibility: *unknown.*

No data available.

- Conclusion based on expert opinion: D90 is a potential alternative, yet more data are required.

Non-phenolic alternatives

An overview of the chemical structures of the non-phenolic alternatives is given in figure 5.

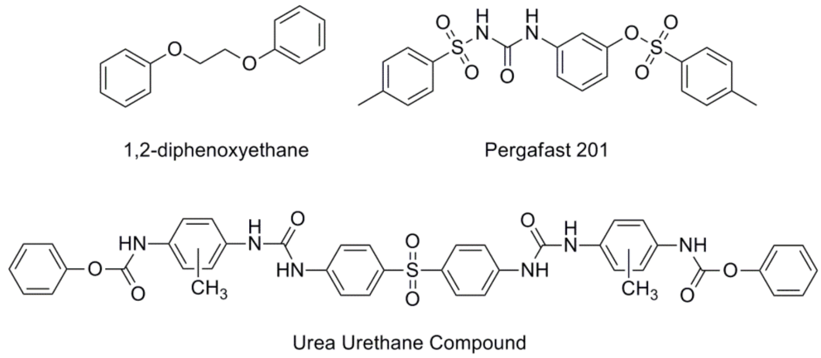


Figure 5: Overview of non-phenolic BPA alternatives.

1,2-diphenoxyethane [104-66-5]

- Availability: *confirmed.*

Based on the REACH registration dossier 1,2-diphenoxyethane can be considered as available.[1]

- Technical feasibility: <u>*none*</u>.

The French restriction proposal states that "Given that 1,2-diphenoxyethane seems to be used in thermal paper, it can be deemed as technically feasible." However, analysis of the patent literature on thermal paper systems shows that 1,2-diphenoxyethane is merely used as heat fusible component in the total formulation.[12] The absence of acid functionalities in the molecule furthermore excludes it from being used as a developer for leuco dyes.

- Economic feasibility: *unknown.*

No data available.

- Conclusion based on expert opinion: Contrary to what is suggested in the French proposal, 1,2-diphenoxyethane is not a developer for leuco dyes, and hence is not an alternative for BPA in thermal paper.

Pergafast 201 [232938-43-1]

- Availability: *confirmed.*

Commercial product from BASF (formerly Ciba).[13]

- Technical feasibility: *confirmed.*

Pergafast 201 is a commercial non-phenolic colour developer for thermal paper. Once the paper is produced, phenol free alternatives have better performance than BPA, because of their higher image stability.

- Economic feasibility: *confirmed.*

Thermal paper with Pergafast is quite common and is the most expensive alternative (usually 10-25% more expensive than BPA based paper).[3] It should be noted that Pergafast 201 is currently only produced by one manufacturer, which means there is no competition regarding price and no possibility for flexibility regarding delivery from multiple suppliers. Whether these high prices and risks of discontinuous supply lead to hesitations by paper manufacturers to substitute to this alternative has not been clarified.[3] Given the complex chemical structure of Pergafast 201, production costs (which of course also depend on scale) will always be higher than those of BPA (expert opinion).

- Conclusion based on expert opinion: Pergafast 201 is a confirmed alternative.

Urea Urethane (UU) [321860-75-7]

- Availability: *feasible.*

According to the French restriction proposal UU is already used in thermal paper, yet mostly as printing stabilizer.[1] UU has not been registered under REACH so far, and production data are not publically available. Recent patents on the use of UU in thermal printing are assigned to Chemipro Kasei Kaisha[14], while older patents are assigned to Asahi Chemical (albeit with the same inventors). This was also observed in a Swedish BPA report.[15]

- Technical feasibility: *feasible.*

UU derivatives have no acidic protons, but are suggested to promote ring cleavage of fluoran dyes, and stabilize the dye/developer complexes.[16,17]

- Economic feasibility: *unknown.*

No data available.

- Conclusion based on expert opinion: UU is a potential alternative, yet more data are required.

General observations

Compared to BPA based paper, image stability is similar or slightly higher for paper based on bisphenol S, higher for D-8 and D-90 and much higher for Pergafast. For customers substituting to thermal paper rolls without BPA, there are no technological challenges, since existing thermal printers can be used without adjustments.[3]

The <u>confirmed</u> technical alternatives are all more expensive than BPA. Thermal paper with Bisphenol S is the most common and cheapest alternative (approx. 5-10% more expensive than BPA based paper). The price for thermal paper with D-8 or D-90 is somewhere in between the price for thermal paper with bisphenol S and Pergafast.[3]

Besides the higher cost for the alternatives compared to BPA, the other negative aspect mentioned by the paper manufacturers was that substituting a developer requires significant adjustments in the thermal paper manufacturing process such as modification in the chemistry of the paper (not only the developer), and quality adjustments. From the collected information, it appears that substitution is not a one-to-one substitution.[3]

Task 2: Completeness check

The following section is a completeness check of the analysis of alternatives as presented in the French restriction proposal. This includes any information available in the public domain on chemical alternatives that are additional to those presented in the restriction proposal. Aim of this action is to review (potential) (bio-based) substance alternatives for the use of BPA in thermal paper.

From the analysis of the technically feasibility of alternatives follows that a number of prerequisites have to be met with regard to physical-chemical properties, in order to consider a substance as a feasible alternative to BPA in thermal paper (according to expert opinion):

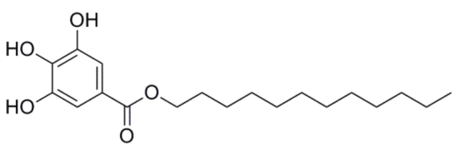
- In case of phenolic alternatives
    - At least one phenolic hydroxyl group (e.g. D8)
    - pKa range and steric hindrance of hydroxyl group comparable to BPA (see hindered phenolic anti-oxidants)
    - Melting point comparable to that of BPA (158-159 °C)
- In case of non-phenolic alternatives
    - Structural similarity with Pergafast 201 and UU: e.g. the presence of urea and urethane functionalities

The list of additional alternatives given below is ordered according to feasibility; i.e. the most feasible alternative is ranked at nr. 1.

Phenolic alternatives

- Gallic acid derivatives.

Although mentioned in the public literature[17] as a known developer for leuco dyes, lauryl gallate [1166-52-5], or other derivatives of gallic acid [149-91-7], have not been mentioned in any of the reports on BPA alternatives.



lauryl gallate

- Availability: *confirmed.*

As a food additive, lauryl gallate is used under the E number E312 as an antioxidant and preservative.[5] Gallic acid is biobased and can be obtained from tannins.

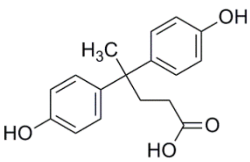
- Technical feasibility: *confirmed.*

Lauryl gallate (m.p. 96 °C) is mentioned in the public literature as a known developer for leuco dyes.[17]

- Economic feasibility: *unknown.*
  Within the limited scope of the project no public economic data could be found.
- Conclusion based on expert opinion: Gallic acid derivatives are feasible alternatives.

- Diphenolic acid derivatives.

Diphenolic acid (4,4-is(p-hydroxyphenyl)pentanoic acid [126-00-1]), is a <u>biobased</u> bisphenol derivative, produced from phenol and levulinic acid [123-76-2]. Levulinic acid is a by-product from many biorefinery processes, as well as the conversion of sugars to HMF (5-hydroxymethylfurfural). According to Blair *et al.* diphenolic acid has at least 10 times less affinity for estrogen receptors than BPA.[18]



diphenolic acid

- Availability: *confirmed.*

Diphenolic acid is a commercial specialty chemical.

- Technical feasibility: *feasible.*

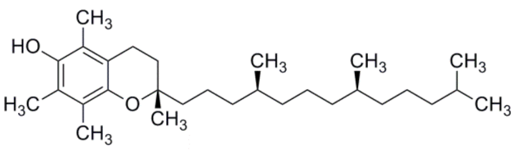
Based on structural similarity to BPA, diphenolic acid (m.p. 168-171 °C), and its esters are potential alternative dye developers.

- Economic feasibility: *unknown.*

Within the limited scope of the project no public economic data could be found.

- Conclusion based on expert opinion: Diphenolic acid derivatives are potential alternatives; more data are required.

- Vitamin E; Tocopherol(s)



a-tocopherol

- Availability: *confirmed.*

Tocopherol(s) are a class of <u>biobased</u> lipophilic antioxidants, which are used in food (E 307) as well as in synthetic polymers (Irganox E201® from BASF).

- Technical feasibility: *unknown.*

The are no public reports on the use of tocopherols as developers for leuco dyes. Since tocopherols have free phenolic hydroxyl groups they can be expected to be active as developers (expert opinion). Potential drawbacks could be steric hindrance of the reactive hydroxyl functionality by the methyl groups (see also hindered phenolic anti-oxidants), and the low melting point (<RT).

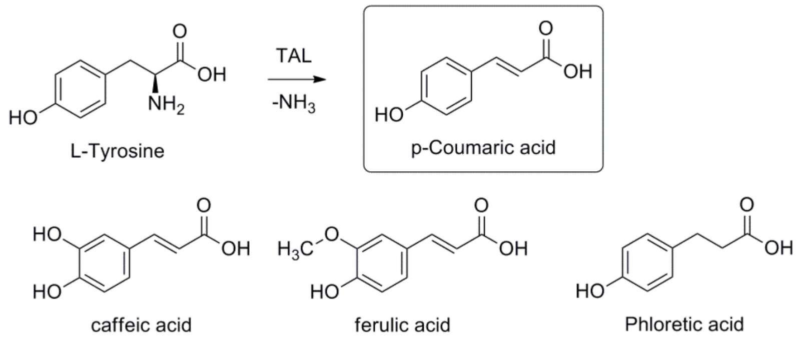
- Economic feasibility: *unknown.*

A potential drawback could be the high price.[19]

- Conclusion based on expert opinion: More data required for assessment.

- Coumaric acid derivatives.

p-Coumaric acid [7400-08-0] and derivatives could also potentially serve as biobased phenolic developer. Coumaric acid is major component of lignin. It can also be formed by deamination of the amino acid L-tyrosine by the tyrosine ammonia lyase enzyme.



- Availability: *unknown.*

Although *p*-coumaric acid and derivatives appear to be available as specialty chemicals, no actual information on availability could be found within the limited scope of the project.

- Technical feasibility: *unknown.*

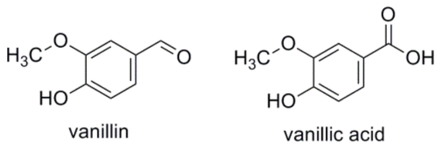
The are no public reports on the use of these substances as developers for leuco dyes. Based on physico-chemical features like the presence of free phenolic hydroxyl groups and sufficiently high melting points these substances (p-coumaric acid 210–213 °C, caffeic acid 223-225 °C, ferulic acid 168-172 °C, phloretic acid 129-131 °C) are potential technical alternatives for BPA.

- Economic feasibility: *unknown.*

Within the limited scope of the project no public economic data could be found.

- Conclusion based on expert opinion: Coumaric acid derivatives are potential alternatives; yet more data are required.

- Vanillin and derivatives.



- Availability: *confirmed.*

Vanillin and derivatives, are biobased phenolics obtained from lignin, an agro-residue from pulp mills and lignocellulosic biorefineries. Vanillin [121-33-5] is a food grade substance. Also vanillic acid [121-34-6] is used as a flavoring agent.[5] The global market for vanillin and ethyl vanillin is placed in the range of 12,000 to 16,000 tonnes per year, with 2,000 tonnes coming from lignin-based vanillin. Production of pure natural vanillin is estimated around 40 tonnes per year.[20]

- Technical feasibility: *unknown.*

The are no public reports on the use of vanillin (m.p. 81-83 °C) or vanillic acid (m.p. 210–213 °C) as developers for leuco dyes. However, based on physico-chemical features like the presence of free phenolic hydroxyl groups and reasonably high melting points these substances are potential technical alternatives for BPA.

- Economic feasibility: *feasible?.*

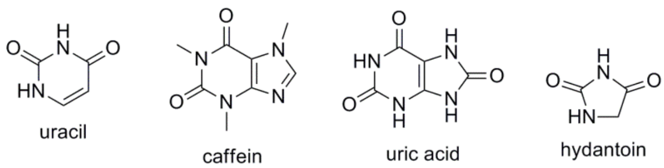
Current synthetic vanillin price was reportedly quoted around $14 to $15 per kilo for large contracts.[20] However, it should be kept in mind that the main application is in flavoring agents and scents, which requires very high purities and hence high purification costs.

- Conclusion based on expert opinion: More data required for assessment. High price could be detrimental.

Non-phenolic alternatives

- BTUM (4,4'-bis(N-carbamoyl-4- methylbenzenesulfonamide) diphenylmethane, [151882-81-4]), which has also been suggested as non-phenolic BPA alternative, can be ruled out as potential alternative based on suspected carcinogenicity and high ecotoxicity.[3,21]

- Uracil type substances.



The two confirmed non-phenolic dye developers, i.e. Pergafast 201 and UU, both contain aromatic urea functionalities, which are apparently necessary for reaction with the leuco dye. In nature activated urea functionalities are present in a wide range of substances.

For instance, the uracil motive is relatively abundant in natural compounds, like in uracil [66-22-8], caffeine [58-08-2] and uric acid [69-93-2], and based on these characteristics could potentially serve as dye developer in thermal paper. Also hydantoin, or glycolylurea [461-72-3] falls into this category. Most of these substances are either biobased or biocompatible, have high melting points, and are (weakly) acidic. All of the substances mentioned here are commercially available specialty chemicals. An in-depth discussion on feasibility of BPA replacement falls outside of the scope of this report.

General remarks on task 2

Several possible biobased alternatives to BPA in thermal paper have been discussed in this section. For most of these substances, the technical feasibility, as well as the effects on human health and environment need to be investigated.
Given the overall feasibility assessment, especially gallic acid derivatives appear highly interesting as BPA alternatives in thermal paper. It is recommended (expert opinion) that these substances be given high priority in further assessment of (biobased) alternatives.

Task 3: Assessment of alternatives of BPA in other applications

The aim of this task is to check whether the alternatives discussed under tasks 1 and 2 are technically feasible alternatives for BPA in polycarbonate (PC) and in epoxy resins.

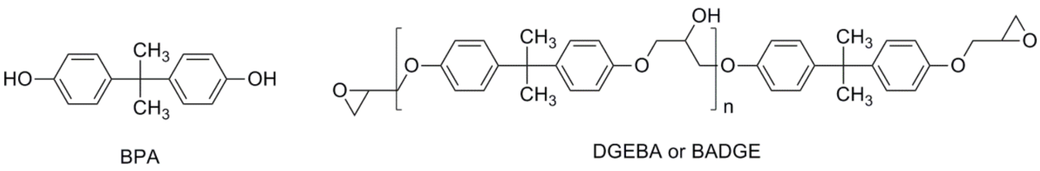


Figure 6: Chemical structures of BPA and DGEBA.

The application of BPA as developer for leuco dyes in thermal paper is based on the presence of weakly acidic phenolic hydroxyl groups, combined with a sufficiently high melting point. However, other applications of BPA, like in PC and epoxy resins, require other physico-chemical properties. For the preparation of polymers a difunctional monomer, with 2 reactive hydroxyl functionalities is required. In the case of PC, BPA is reacted with either phosgene ($COCl_2$) or diphenyl carbonate to give the polycarbonate; a high performance material with a high T_g (150 °C), high thermal stability, high optical transparency and very high toughness. Hence BPA alternatives should be rigid and thermally stable. Bisphenol A diglycidyl ether (DGEBA) is obtained by reacting BPA with epichlorohydrin, giving an oligomeric product with an epoxy number of ≥ 2. While for PC and epoxy resins rigid aliphatic diols like the biobased isosorbide [652-67-5] can be alternatives to BPA, this is not the case for application in thermal paper, since the acidity of aliphatic diols is too low for developing the leuco dye.
Table 1 shows that out of the alternatives discussed in task 1 in this report only difunctional, rigid bisphenol derivatives are feasible alternatives for BPA in PC or epoxies. Unfortunately, these substances display similar endocrine effects as BPA. The list of potential alternatives discussed in task 2 contains only two difunctional substances, i.e. diphenolic acid (and derivatives) and gallic acid derivatives (actually trifunctional). Both have been shown to be applicable in epoxy resins, while diphenolic acid (and derivatives) has been applied in polycarbonates.

Table 1: feasibility of BPA alternatives in PC or epoxies (expert opinion).

Substance	**Reactive groups**	**PC alternative**	**Epoxy alternative**
Task 1			
BPS	2 OH	Yes	Yes
BPF	2 OH	Doubtful; thermal stability issues	Yes
BPAP	2 OH	Yes	Yes
D8	1 OH	No	No

Substance	**Reactive groups**	**PC alternative**	**Epoxy alternative**
TG-SA	2 OH	Doubtful due to pendant groups	Doubtful due to pendant groups
DD70	2 OH	No, too flexible	No, too flexible, thioether stability issues
D90	2 OH	No, too flexible	No, too flexible
1,2-diphenoxyethane	0	No	No
Pergafast 201	?	No	No, incompatible with epichlorohydrin[22]
UU	?	No	No, incompatible with epichlorohydrin[22]
Task 2			
Gallic acid	3 OH	No, too high functionality which gives rise to branching	Yes[23]
Diphenolic acid	2 OH	Yes	Yes

3 Conclusions

Task 1: Assessment of the selected BPA alternatives as developer in thermal paper.

- Of the seven phenolic substances listed in the French proposal only Bisphenol S and D8 can be considered as feasible based on availability (commercial products), technical feasibility (already applied as developer in thermal paper), and economic feasibility (commercial product with known prices).
- However, given the very high structural similarity to BPA (and estradiol), a similar endocrine disrupting potential can be expected, or is already confirmed, for these bisphenol derivatives. This makes it doubtful whether substitution by these substances will bring any benefits to public health and environment.
- Out of the three non-phenolic substances listed, at least one, i.e. 1,2-diphenoxyethane, is not active as a dye developer in thermal paper, and as such should be removed from the list.
- The other two non-phenolic substances, i.e. Pergafast 201 and UU can be considered as feasible. These substances appear to have no endocrine disrupting effects.
- Pergafast 201 is a commercial product, which is applied as developer in thermal paper. Potential drawbacks of this substance are the significantly higher price, the fact that there is only one supplier, and the potential ecotoxicity (persistence and aquatic toxicity)
- For UU technical feasibility appears sufficient. The lack of data on availability (producer(s), tonnage) and prices make it difficult to assess these parameters.
- Since the aim of the French restriction proposal is to reduce human exposure to endocrine disruptors, only replacement of BPA in thermal paper by the non-phenolic alternatives Pergafast 201 and UU will have beneficial effects on human health.

Task 2: Completeness check.

The completeness check shows that especially for phenolic type substances, various potential (biobased) alternatives have not been discussed in previous proposals. A prime example here is the group of gallic acid derivatives, which are known developers for leuco dyes according to the scientific literature. Furthermore, biobased diphenolic acid (and derivatives) could also be a potential alternative to BPA. Various other biobased substances have been identified as potential alternatives to BPA, yet a proper assessment of their viability will require significant research efforts.

Task 3: Assessment of alternatives of BPA in other applications.

Of the ten alternatives for BPA in thermal paper listed in the French proposal, only two, i.e. BPS and BPAP are feasible for application in polycarbonate or epoxy resins. Unfortunately, these substances are highly similar to BPA, and therefore substitution would probably not lead to significant health benefits.

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