Environmental and Regulatory Aspects of Dry Toners

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Abstract

Recent publications in scientific but as well non-scientific journals and magazines have raised the question of potential hazardous emissions from copiers and printers during its life-cycle. In this contribution the key environmental aspects of modern dry toners are compiled. Particular emphasis is given to the requirements as described in the various application families of the German Blue Angel eco-label (Blauer Engel www.blauer-engel.de, English and German information are available). This label was established in 1978 as the oldest so-called third-party voluntary "Seal of Approval" distinguishing environmentally improved products from ordinary ones. Since the amendment in January / February 2004 not only the use of heavy metals, azo-dyes and other hazardous substances as evidenced by negative AMES test in toner are prohibited , but also maximum limits for emissions from toner have been defined for the first time. Maximum emission levels were established for volatile organic compounds, such as, in particular, benzene and styrene, for ozone and for dust. New stricter environmental requirements will be applied with the next amendment expected for the beginning of 2007.

The exact requirements, test procedures and protocols for toner producers and raw material suppliers will be described in this contribution. The impact of these environmental questions on toner formulation and raw material selection will be described for several cases with particular emphasis on cyclic olefin copolymers a new, eco-friendly class hydrocarbon toner binder resins.

Introduction

Today most offices are equipped with personal computers and monochrome black laser printers. In parallel color printers and copiers are getting cheaper, thus entering ordinary offices and will soon make their way into private homes [1].

As electrophotographic devices are becoming omnipresent in our normal life the discussion in scientific and non scientific articles has recently started if and to what extent laser printers and copiers make a substantial contribution to indoor air pollution through volatile organic carbons and thus represent a threat for the human health [2], [3], [4], [5]. Although it is evident that toners do not represent an acute danger for the human health and the long term risk in comparison to other sources of air pollution is definitely small, consumer in Europe, especially in Germany, and in Japan, are concerned about the ingredients that a present in some toner formulation. For example tin organic components like dibutyl tin (DBT) and tributyl tin (TBT) already banned for the use as marine safety coatings for ships have been found in significant amounts in various color toners of famous printer manufactures [6]. In parallel the absence of such potentially hazardous chemicals in selected toner formulations demonstrate that they are not essential for good end use performance. Although a society can not ban the use of such ingredients with unknown risk status the enlightened consumer should at least know the best of a class products with respect to the environment and decide by its own choice to buy them or not. This is the starting point of the Blue Angel environmental label.

Within this article the exact requirements and the detailed test procedures of the Blue Angel ecolabel for NIP products will be described. Furthermore future development directions for toner producers and raw materials suppliers will be explained for the particular case of cyclic olefin copolymers, a new, eco-friendly class of hydrocarbon toner binder resins.

The Environmental Blue Angel Label

The Blue Angel environmental label was established in 1978 and was the first label under the category "Seal of Approval". Since then several additional labels like Green Seal for USA, Eco Mark in Japan, Environmental Choice for Canada and White Swan for Scandinavia have been introduced as a "soft instrument for environmental policy" [7], [8]. It gives a simple classification for the end user distinguishing environmentally improved products from ordinary one.

The Blue Angel is a so called voluntary label meaning that the producer is free to decide according to its marketing needs whether to expose a product to the basic criteria defined there or not. Blue Angel classification has shown to give the manufacture a competitive advantage in order to sell more of a product for a higher price.

As the approval is verified by an independent source according to a standardized evaluation process eco labels like Blue Angel are classified as so called third party labels.

Blue Angel and NIP

The following application families are relevant for the non-impact printing industry:

- UZ 55: Reusable Toner Modules, amended in February 2006
- UZ 85: Printers, amended in January 2005
- UZ 114: Multifunctional Devices, amended in January 2005
- UZ 122: Copiers, amended in June 2006

In general the goal of Blue Angel is to prevent pollutants, emissions and waste, to limit energy consumption during use as much as possible and to allow recycling of used devices. Thus the Blue Angel environmental label is awarded to products with the following properties:

- Lower power consumption especially during idle running than comparable products.
- Devices have long lifetimes, construction meets the principle of recycling, all possibilities of reuse and recycling are realized.

- The use of pollutants is prevented as much as technically reasonable.
- Low noise generation during use.
- Supply appropriate customer information comprising indications for power savings, noise development, special features to consider for set-up, handling of consumables and appropriate disposals of devices and consumables.

With the amendments in January / February 2004 which were confirmed by the following amendments in 2005/2006 for the first time not only requirements for the print engine were defined but as well detailed specifications for approved xerographic toner were given.

Blue Angel Toner Requirements

According to the latest amendments the use of the hazardous substances as shown in figure 1 are prohibited.

Prohibited Hazardous Substances in Toner

Use of substances is prohibited which are classified in 67/584/EWG appendix I as:
Carcinogenic acc. to EU Category Carc. Cat. 1, Carc. Cat. 2, Carc. Cat. 3
Mutagenic acc. to EU Category Mut. Cat. 1, Mut. Cat. 2, Mut. Cat. 3 or
Endanger for reproduction acc. to EU Category Repr. Cat. 1, Repr. Cat. 2, Repr. Cat. 3
And marked with the following risk phrases acc. appendix III and VI

R26:	very toxic if inhaled
R27:	very toxic in case of skin contact
R40:	suspect of carcinogenic effect
R42:	sensitization after inhalation
R45:	may cause cancer
R46:	may cause genetic damage
R48:	may cause serious health hazard for long expositions
R49:	may cause cancer if inhaled
R60:	may impair reproduction
R61:	may be harmful to embryo
R62:	may possible impair reproduction
R63:	may possible be harmful to embryo
R64:	may be harmful to baby via mother's milk
R68:	possible irreversible damage

Or classified as carcinogenic, mutagenic or endanger for reproduction acc. TRGS 905
Or classification with R 43: sensitization in case of skin contact for the whole toner product
And AMES test with showing no activity so called negative test result.

Figure 1: *Prohibited hazardous substances in toner.*

In addition the use of the heavy metals mercury, cadmium, lead and chromium (VI) in toner products complying with the Blue Angel requirements is prohibited. The cobalt and nickel content has to be reduced according to the minimization rule as low as technically possible and economically feasible. In the amendment of UZ 55 from February 2004 it was further announced that the presence of tin organic components in toner powders sometimes used as catalysts in the polyester polycondensation reaction will be banned in future amendments although this was not done with the most recent ones in 2006.

Furthermore the use of azo colorants (dyes and pigments) which may release carcinogenic amines according to 2002/61/EG (TRGS 614) is not allowed.

The applicant has to proof that his product meets the award criteria by a certificate from an independent test institute or with a declaration of an authorized person from the applicant. An AMES test showing no activity which is called " negative" result has to be done in any case. If the toner formulation is changed for an existing product a new test certificate has to be presented.

In the amendments from 2004 maximum emission levels of toner materials used in a given printer or copier and thus for a defined printing speed were specified for the first time. The maximum allowed emission levels are given in table 1.

Table 1: Maximum emission levels of toner.

Substance	Emission Rate Copy Mode mg / h
TVOC	10
Benzene	0.05
Styrene	1.0
Ozone	2.0
Dust	4.0

As shown in table 1 toner powders are tested for TVOC, benzene, styrene, ozone and dust emissions in the Copy Phase. During the Ready Mode TVOC is limited to 1 mg/h for desk devices and to 3 mg/h for stand alone devices. Among these pollutants benzene is assessed as most critical because it is known to cause cancer in humans. For these substances there is often no limit established below which they (in this case benzene) can be handled without risk for human beings. For substances classified like this in Germany the minimization rule applies meaning that its content has to be as low as technically possible and economically feasible.

The test procedure for emissions from toner is described in appendix 6 of the Blue Angel standard which is only available as pdf-file on the homepage. It is done in a relatively small "environmental chamber" of usually 1 m3 at 23°C and <30 % r.H. at the beginning of the printing phase and an elevated air exchange rates of 4-5 h-1 to avoid condensation of water on the chamber walls and thus completely wrong results for water soluble VOCs. The measurement procedure involves sampling on the absorbent Tenax™ TA, subsequent thermodesoprtion and detection with GC / MS coupling. A blank value before charging the environmental chamber is done first. Then the printer is conditioned for 1 h and the second measurement at the end of the 1 hour Ready Mode phase is done. It is followed by a printing phase with 500 copies for 10 to 30 minutes with a standard pattern of 9.5 or 5 % page coverage in the case of black toner. Sampling is done at the very end to ensure that the equilibrium value is reached. For color toner a different print pattern is employed.

Blue Angel standard requires that testing is done by an appropriate test institute. So far only two institutes namely Bundesanstalt für Materialwirtschaft (BAM) and Landesgewerbeanstalt Bayern (LGA) are notified bodies for that test [9].

Complementary Testing

As environmental tests are quite complex and costly in the range of 5,000 EUR per toner sample LGA proposes an initial prescreening of the black toner powder with headspace GC at 90 °C and other methods. The limits as presented in figure 2 were established.

Test Criteria of LGA QualiTest GmbH for Black Toner Powder Material Characterization for Label "Tested for Contaminants"

No.	Test	Limit
1.	Volatile Organic Emissions	
1.1	TVOC	< 300 mg/kg
1.2	Benzene	< 0.35 mg/kg
1.3	Styrene	< 40 mg/kg
1.4	CMT*	< 1 mg/kg
2.	Heavy Metals	
2.1	Cobalt	< 25 mg/kg
2.2	Nickel	< 70 mg/kg
2.3	Chrom (VI)	< 1 mg/kg
3.	1-Nitropyrene	< 0.5 mg/kg
4.	Benzo(a)pyrene	< 0.5 mg/kg
5.	Tin Organic Substances	
5.1	Sum of all Sn Organics	< 500 µg/kg
5.2	TBT (Tributyltin)	< 50 µg/kg

*CMT= Carcinogenic, Mutagenic, Teratogenic

If the material fulfills this certification criteria then the subsequent emission test in the environmental chamber is done.

Figure 2: *Material Test Criteria of LGA.*

As shown in figure 2 beside volatile organic emissions heavy metals and other substances are tested, too. Please be aware that limiting values for tin organic components as announced for future amendments are already defined there.

Such a material characterization is much easier and priced at around 1,000 EUR / sample. If the black toner sample passes this initial screening phase then subsequent testing for emissions in an environmental chamber is done.

In order to support aftermarket toner manufacturers to adapt these limiting values and to demonstrate their customers that their toner fulfill the same requirements as OEM toner LGA offered a certificate "Tested for Pollutants". This test certificate became obsolete with the amendment of UZ 55 and will soon be substituted by the Blue Angel mark.

It has to be noted that different material specifications for toner products have been set up by other entities, e.g. the German professional trade organization (Hauptverband der gewerblichen Berufsgenossenschaften) has published its own material specifications for toner products to receive the BG label "Tested for Pollutants" in December 2004 [10] which are presented in figure 3. Please note that the GC measurement is done after desorption for 30 minutes at 130°C and is thus not directly comparable with that of LGA.

But other Test Criteria under Different Conditions do exist as well, e.g. HVBG Label "Tested for Contaminants"

No.	Test	Limit
1.	Volatile Organic Emissions	
1.1	TVOC	< 1000 mg/kg
1.2	Benzene	< 1 mg/kg
1.3	Styrene	< 40 mg/kg
1.4	Toluene	< 40 mg/kg
1.5	Ethlybenzene	< 40 mg/kg
1.6	Xylene	< 40 mg/kg
2.	Heavy Metals	
2.1	Cadmium	< 5 mg/kg
2.2	Cobalt	< 25 mg/kg
2.3	Nickel	< 70 mg/kg
2.4	Lead	< 25 mg/kg
2.5	Chrom	< 1 mg/kg
2.6	Sn-organics	< 5 mg/kg

HVBG = Hauptverband der gewerblichen Berufsgenossenschaften
German professional trade organization

Same critical substances identified,
Limits for Sn catalysts less severe

Figure 3: *Material Test Criteria of HVBG.*

As seen in figure 3 the same critical substances in toner materials are identified and screened for this label although limiting values for tin organic components are significantly higher than that of LGA.

First Test Results for Xerographic Toner

First test results show that a large number of modern copiers and printer already fulfill the requirements of the Blue Angel standard [5], [11]. Most critical for the human health so far are benzene emissions which exceed the emission level limit of 0.05 mg/h = 0.8 g/min for 10 printers and copiers for the 65 devices studied of far corresponding to about 15%. By comparison between benzene content in the toner and benzene emissions from the printer it was shown that toner are the most important sources for benzene release. Surprisingly more benzene is emitted during printing than actually contained in the toner meaning that additional benzene is generated during the electrophotographic printing process.

A statistical evaluation of more than 100 toner sample analysis is given in table 2.

Table 2: Recent test result for toner of Jungnickel et al.

Component	Sample Number	Max /mg/kg	Average / mg/kg	Median / mg/kg
Styrene	137	860	75	32
Benzene	137	120	3	<0.1
TVOC	102	1330	256	170

Table 2 reveals that the styrene and TVOC content exceed the internal limit established by LGA for a significant amount of commercial toner samples. In order to take precautions it is highly recommended to reduce the emission levels of these toners.

Preliminary test results indicate that cyclic olefin copolymers available from Topas Advanced Polymers under the trade name Topas® COC and toner made from these binder resins comply well with the requirements of Blue Angel certification [12], [13]. In particular Topas COC binder resins show the following beneficial eco-friendly properties:

- Topas COC polymers are made from ethylene and the cyclic olefin norbornene, are consequently fully hydrocarbon in nature and do not carry any functional groups. It is thus estimated that these materials should show a lower risk for carcinogens or endocrine disrupter potential toners if carefully processed. Such issues are currently discussed in the literature for styrene monomers normally formed during extrusion of styrene-acrylic resins at elevated temperatures or for bisphenol A which forms the base ingredient for polycondensation polyester binders.
- Due to the fully continuous production method and an efficient thermal work-up procedure Topas COC polymers show very low total volatile organic

carbon contents as already confirmed by several analysis of independent test institutes or companies. Detailed analytical data are available on request.

- Topas COC materials are polymerized with the help of minor amounts of zircon based metallocene catalysts and aluminum components which are efficiently separated from the polymer in the subsequent production process to further reduce the catalyst residues to give a purer product with superior optical properties. In particular no hazardous heavy metals chemical compounds like tin organic components still used sometimes for the production of polyester toner bind resins are used.

Although Topas COC based toner formulations should show superior eco-friendly properties in comparison to other toners it is important to point out that every toner manufacturer has to demonstrate that his propriety toner complies well with the necessary requirements. In fact other toner ingredients like pigments, CCA and waxes although used only in small quantities or the toner production process may significantly contribute to the environmental behavior of the final toner and thus have to be as well selected with ultimate care.

Future Developments

So far various international printer and especially German aftermarket toner resellers have NIP products that carry the Blue Angel eco label. A complete list is available on the internet [8]. As governmental organizations which are major consumers of toner are asked to use the environmentally best toner modules if different products at comparable costs are available it is estimated that this number will grow continuously.

In the probable case that toner with low emission will become standard in the near future these requirements will have a direct impact on toner manufactures as they are responsible that their products are in compliance with the rules. Toner producers will then require their potential raw material suppliers to check if their products will fulfill current and future emission levels. Such an approach is known in the medical industry where ingredients are not even considered for the development phase unless the supplier has proven that his product is in agreement with the corresponding pharmaceutical approval needs. The test protocols as described in figures 2 and 3 gives toner suppliers an excellent, straight forward opportunity to respond to this demand.

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Author Biography

Klaus Berger received his Ph.D. in Physical Chemistry from the university of Paderborn, Germany, in 1995. He then worked on biodegradable polymers at the Federal Institute for Cereal, Potato and Starch Research in Detmold, Germany and on the rheological properties of associating polymer solutions at the Laboratory for Ultrasounds and the Dynamics of Complex Fluids in Strasbourg, France. In 1997 he joined the research and development group of Topas® COC within Hoechst, later Celanese/Ticona and now within Topas Advanced Polymers which was established in 2006. There is currently working on Topas® COC toner binder resins for high quality printing in a fully equipped state-of-the-art polymer and toner lab. He is a member of IS&T.

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