PET Bottle Flake Decontamination Processes to Achieve Approval for Direct Food Contact

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4th China Int'l Recycled Polyester Fiber Market & Tech Forum
Sept. 2-4, 2008, Hangzhou, Zhejiang Province, China

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1. Decontamination of PET – Introduction

The recycling of PET packaging materials like bottles or film back to food application again by mechanical cleaning, re-pelletizing and molecular weight reconstitution requires high food grade purity. This technology which is called bottle to bottle (B-2-B) recycling is the most applied bottle recycling technology far ahead of chemical recycling and multilayer application of R-PET

Today the B-2-B-recycling is significantly applied and developed in USA and Europe, first plants in Asia. This technology is expected to be introduced also in China within the coming years.

Based on the rules of FDA and country governments very limited kinds of chemical species and concentrations only are allowed to be present in PET resin for food application.

All approved monomers, co-monomers or additives and the related extraction limits of FDA fore instance are described in details under USA Code of Federal Regulations – Food and Drugs 21 CFR Ch. I § 177.1630, details *see http://edocket.access.gpo.gov/cfr_2003/aprqtr/pdf/21cfr177.1630.pdf]*

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During dedicated applications bottle wall and film are absorbing some amounts of the content of packed materials like flavor, oil, color or solvents.

The convenience of the unbreakable and transparent polyester bottle and its everywhere availability ends up with any kind of undesired uses like for instance storage of motor oil, fuel, fertilizer or agriculture chemicals. These substances are often also left back in the wasted bottles.

To remove all possible contaminants migrated into the bottle wall and contaminant residues in the bottle volume a number of different techniques and technologies are developed.

Pioneers of this process development are US-companies like Hoechst –Celanese, Johnson Control or the former polyester producer Goodyear.

Today the number of decontamination processes is growing with the growth of the PET recycling industry. Well known names are for instance Buehler-B-2-B-Process or the flake decontamination by URRC

DEFINITION:

Contaminants are polyester process foreign chemical substances which are penetrating into the bottle wall by migration (diffusion).

Depending on their solubility in polyester and chemical nature, temperature, penetration time and concentration the polyester matrix ingest such substances until their saturation concentration is achieved.

Decontamination is the reverse process and depends on temperature, treatment time, concentration difference between polyester matrix and decontamination medium (gas, vacuum, washing liquid) and dimension (diffusion length) of polyester matrix.

Contamination and decontamination are following in general the Fick`s Laws of Diffusion.

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2. Common Contaminants

The variety of contaminants is significantly increased during the last decade. One reason is the introduction of PET packaging materials to nearly all kind of commonly used liquids like, eatable oil, household chemicals, detergents, health care products, paints, drugs and agricultural chemicals.

Out of these products one can summarize the following groups of chemicals

~ low boiling hydrocarbons, water insoluble – e.g. pentane, fuel, benzene
~ high boiling hydrocarbons, water insoluble – e.g. motor oil, diesel
~ low boiling solvents, water soluble – e.g. acetone, methanol, ethanol
~ high boiling solvents, water soluble – e.g. glycol, glycerin
~ fragrant chemicals and flavor substances
~ solids, water soluble – e.g. sugar, NaCl, fertilizer
~ solids, water insoluble – e.g. pesticides,
~ heavy metals

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3. Steps of Decontamination

~ Collection

One highly efficient “decontamination” to avoid misuse and to circumvent expendable cleaning is

-the recycling of bottles out of the returnable and reusable bottle circuit-

This is instead of collection the selection of used bottles

This is useful in EU-countries or Scandinavia where such kind of deposit systems are established. The bottles will be automatically removed from the circuit after a fixed period of round trips or by automatic detection of scratches or damages.

Provided storage and transport of those bottles is done separated from other collected bottles the contamination is nearly impossible

~ Flake Production

During flake production a number of technology steps are defined to remove all kinds of possible contaminants like:

pre-sorting by applying highly automated systems which are sniffing the content of each bottle by rapid chemical trace analysis. Such kind of technology is for instance applied by the new KRONES bottle recycling process. Target is to avoid intermingling of contaminated bottles to reach lowest contamination contents.

bottle pre washing prior cutting – processing step is removing all coarse and by chance intermingled impurities and contaminants, mainly from the bottle outer surface

wet pre-cutting – cutting and washing at the same time is providing a high efficient removal of all kind undesired contaminants

hot-wash – among all wet treatments the hot or hot+caustic wash process is removing all contaminant from the surface and depending on treatment time and temperature also a substantial amount of low boiling contaminants from polymer matrix

 # Flake treatment with supercritical fluids

One specific decontamination process is to treat the PET-flakes for instance with supercritical CO_2. Positive is high decontamination effectiveness, negative the relative high process cost

 # Flake crystallization and pre-drying – during conventional flake treatment at 140 – 160°C under air substantial amounts of volatile contaminants are removed, especially the large flake surface supports decontamination. There are processes described where even the purging of storage silos by air of slightly increased temperature (~70°C) is supporting the decontamination

 # Flake SSP – some processes are treating the flakes under vacuum of about 1 mbar at 170 – 200°C. This process in increasing the IV and at the same time significant amounts of contaminants are removed

~ Flake Conversion to Pellets

 # Flake extrusion under vacuum – most of the currently operating recycling processes applying extrusion under vacuum. From single screw via double screw to multi-screw and multi-rotation-systems the melt surface area renewal is increasing. At the same time the decontamination efficiency is increasing in the same sequence

~ Partial glycolysis and re-polycondensation

One special case of decontamination takes place during partial glycolysis and re-polycondensation. This process is also counted as “chemical recycling”

In most of the cases PET flakes are extruded in presence of about 0,5% MEG to glycolyse and depolymerize the polyester backbone.

This glycolysis product is fine filtered and directly fed to a polycondensation line prior the finisher.

The addition of glycolysis product is commonly between 5 and 30%. Because of the high vacuum, long treatment time and high temperature the decontamination via this route is excellent.

This kind of decontamination is exclusively applied by PET resin producers, especially in USA forced by Coca Cola.

~ Solid State Treatment of Pellets

Every pellet production process includes another thermal treatment like crystallization, drying and SSP. All those processes are supporting the removal of volatile substances significantly. Well known is the removal of acetaldehyde to trace concentration of < 1 ppm

Crystallization – the crystallization temperature of 150° - 180°C and the residence time of about 30 min supports decontamination

Drying – temperature treatment between 150 and 180°C for 4 – 8 hours in presence of dry air or dry nitrogen is removing volatile contaminants forceful

Solid State Polycondensation – temperature treatment between 190 and 220°C under vacuum (1 mbar) or in presence of dry nitrogen is one of the most sufficient thermal treatment to remove volatile contaminants. High processing duration (6 – 12 hours) combined with high temperature are optimal conditions for decontamination

4. Efficiency comparison of processing steps

Comparing all of the listed steps of decontamination the following efficiency categories are to summarize**:**

Low efficient decontamination:

~ flakes air purging
~ flake / pellet crystallization
~ flakes cold wash

Medium efficient decontamination

~ flake / pellet drying
~ flake hot wash
~ single screw extrusion, degassing only

High efficient decontamination

~ supercritical extraction
~ vacuum extrusion, efficiency increase like: single screw→ twin screw→ multi screw
~ flake and pellet SSP under vacuum and under dry gas (N2) treatment
~ vacuum melt polycondensation

4. Efficiency comparison of processing steps

To design a production-scale recycling process of high decontamination efficiency different combinations of decontamination strategies are chosen in the industrial practice. Some of these processes are integrated from bottle presorting to bottle grade pellets via washing, grinding, extrusion and SSP and some processes are using PET flakes from the market as start material.

Some Examples:

Bühler Process: Flakes (in-house or market) → multi screw extruder and vacuum degassing → pellet crystallization and SSP

Krones Process: Bottle sorting by mass spectroscopy, washing incl. hot wash, flake SSP

URRC Process: Flake production (sorting, cold+hot wash) → flake surface alkaline treatment and thermal decontamination under maintenance of IV → washing under removal of alkaline → flake drying

5. How to verify the Effectiveness of Decontamination?

Caused by the large and still rapidly increasing number of possible contaminants the verification of decontamination effectiveness of recycling processes is a scientific and technical difficulty. Problem is to simulate all possible contaminants as well as the conditions of contamination and decontamination. The solution provides the so called "Challenge Test" where

~ Challenge Test

"The FDA has specified a "Challenge Test" procedure to allow recycling processes to be validated as being capable of removing severe contamination from bottles that have been deliberately contaminated in a controlled way. This provides regulatory bodies with assurance that the much lower level of contamination present in collected bottles will be readily removed to levels that present negligible risks to consumers"

{[*1] source http://www.ce-pip.com/docs/FOOD-GRADEAPPROVAL-UK.pdf - by WARP}*

To simulate the large number of possible contaminants four example chemical properties are selected with the following description:

A volatile, non-polar organic substance
A volatile, polar organic substance
A non-volatile, non-polar substance
A non-volatile, polar organic substance.

Table 1 is showing a selection of suggested substances [1]

Volatile Polar	Non-Volatile Polar	Volatile Non-Polar	Non-Volatile Non-Polar	Heavy Metal
Chloroform	Benzophenone	Toluene	Tetracosane	Copper(II) 2-ethylhexanoate
Chlorobenzene	Methyl salicylate		Lindane	
1,1,1-Trichloroethane			Methyl stearate	
Diethyl ketone			Phenylcyclohexane	
			1-Phenyldecane	
			2,4,6-Trichloroanisole	

To perform the challenge test a substantial amount of test flakes are contaminated with a cocktail of the above collected chemicals. In table 2 an example text cocktail is described.

Tabel 2: Examples of Minimum Concentrations of Contaminants in a Surrogate Cocktail [1]

Contaminant	Concentration
Chloroform (volatile polar)	10% v/v_a
Toluene (volatile non-polar)	10% v/v_a
Benzophenone (non-volatile polar)	1% v/v_a
Tetracosane or Lindane (non-volatile non-polar)	1% w/w_b
Hexane or Heptane (as overall solvent for cocktail)	68% v/v_a

v/v_a – volume of contaminant per unit volume of entire cocktail
w/w_b – mass of surrogate per unit mass of entire cocktail

To penetrate the surrogate cocktail to the polyester flakes similar to practical conditions the flake/surrogate-cocktail blend is sealed stored at 40°C for two weeks under frequent agitation. After this treatment the surrogate cocktail si drained from the flakes, the flakes are rinsed with clean water. After dewatering by centrifuge the flaks are ready to use in the decontamination test.

~ **Analytics and Regulatory Support**

The Fraunhofer Institute IVV (Freising, Germany) has developed analytical procedures and tests for flake, pellet and packaging products to detect the level of decontamination of the PET material and the migration of any species from packaging into food products.

Once special part of this analytical works is the trace analysis of contaminants after the PET flake challenge test. Because of the complexity of the challenge test procedure and the belonging trace analysis it is recommended to use the service of IVV to perform a meaningful and FDA accepted challenge test *[http://www.ivv.fhg.de/load.html?/mainframes/english/service/service1_index.html]*

Besides the technique of challenge test sample production and chemical analysis the IVV is also supporting the whole approval process.

Similar support is provided by the law firm Keller&Heckmann *[http://www.khlaw.com/]*

Result of the describes testing works is a letter of no objections by FDA. Additional it is important to observe also the local governmental rules and regulations as well as the approvals of the brand owners like Coca Cola or P&G

6. Regulatory Background

~ FDA

“Threshold of Regulation**- USA**

Plastics for food contact are always evaluated for any migration that might occur when in contact with food material.

Migrating substances are considered to be food additives.

“Threshold of Regulation” -a level below which the probable exposure to a potentially toxic substance is a negligible risk (defined as 0.5ppb in daily diet)

US FDA Validation of Recycling Processes

Any recycling process must demonstrate its ability to remove potential contaminants due to consumer misuse.

A series of representative chemicals or their surrogates are used to spike PET flake in a “Challenge Test”.

100% of flake is contaminated for 2 weeks at 40 deg C. (Flake absorb up to 10 times more contaminants than bottles)

Mathematical migration modeling is now accepted instead of some testing and approvals.” *{[2] source: http://staff.bath.ac.uk/ensmns/Seminars/2006-07/20070411.pdf}*

„**US-**FDA “Challenge Test” for Recycling Processes

“Challenge Test” procedure validation as being capable of removing severe contamination from bottles to below the “level of regulation”

Provides assurance that much lower levels of contamination in collected bottles will be removed to negligible risk levels.

From February 1990 to June 2008,
83 “letters of non-objection” have been issued
17 chemical processes and 6 physical recycling processes for rPET
[source: http://www.cfsan.fda.gov/~dms/opa-recy.html]

The chemical recycling no longer requires FDA accreditation.“ *[2]*

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7. Summary

~ Mayor hurdle of the usage of bottles and food packaging made of recycled PET are organic chemical substances which are migrating during regular use or forced by misuse during the first life of the packaging material into the bottle wall (polymer matrix).

~ To guaranty that the usage of recycled PET as food packaging material is completely harmless to the consumer all migrated substances must be removed during the recycling process. As threshold of contamination FDA set a limit of < 0,5 ppb migration to the foodstuff packed in recycled PET.

~ There is a broad range of decontamination techniques whereas melt treatment under vacuum, solid state polycondensation, solid state heat treatment and supercritical extraction are the most efficient one.

~ To evaluate the efficiency of the selected recycling technology FDA introduced the challenge test to demonstrate under worst case conditions the capability to remove contaminants to the threshold of regulation.

~ Professional support in conducting the challenge test and to apply for the FDA approval is provided by companies like Fraunhofer Institute (IVV) or Keller+Heckmann.

~ Besides FDA the local governmental regulations are to observe

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