# Achieving REACH compliance for reaction products of acetic anhydride and adipic acid used in starch modifaction

## Whitepaper

This whitepaper is about the REACH registration of reaction products of acetic anhydride and adipic acid which are commonly used in the acetylation and Cross-Binding of starch based materials.

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AD International | REACHLAW

**ABOUT THE AUTHOR**

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Marco de Kraa graduated from the University of Leiden with a degree in Analytical Chemistry. In his career at AD International BV Marco has worked in various roles, starting in R&D, later as a laboratory manager and now for more then 15 years as SHEQ Manager. Marco has followed the debates and progress of REACH from the early stages and has more than seven years of knowledge to ensure successful REACH implementation. He supports the objectives of REACH and continuously works on REACH compliance matters at AD International BV.

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## EXECUTIVE SUMMARY

REACH, the EU Regulation on Chemicals and their safe use (EC 1907/2006) came into force on the 1st of June 2007. The food industry interprets REACH Regulation's exemptions as not applying to processing aids, chemical intermediates and reagents used in the EU manufacture of food and feed but that are not intended themselves as food or feed ingredients. Reaction products of acetic anhydride and adipic acid are commonly used for starch modification. After looking more closely at the available literature and additional testing using for example IR spectral analyses, AD International BV in conjunction with independent global consultancy firm REACHLaw has come to the conclusion that the reaction products of acetic anhydride and adipic acid obtained during starch modification is a new substance and as such is subject to the registration process as described in the REACH Regulation. AD international BV has successfully registered this product as Lead Registrant under number 01-2120115217-67-0000.

## 1. WHAT IS REACH

REACH is the acronym used for the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) Regulation (EC) 1907/2006[i]. This regulation is by far the most significant piece of chemicals legislation to be implemented in recent years and imposes large obligations on the majority of manufacturers, importers and downstream users of chemicals within the EU.

REACH came into force on June 1st 2007. It is a regulation, not a directive, and so it is being implemented across all EU member states at the same time. REACH has also been adopted by Iceland, Liechtenstein and Norway who are not members of EU but part of the European Economic Area.

REACH aims:

- to improve the protection of human health and the environment from the risks of chemicals, and
- enhance the competitiveness of the EU chemicals industry, by promoting its reputation as a responsible industry and encouraging innovation.

There are an estimated 100,000 substances commonly in use in the EU. Many of these have been in use for a long time, but there is very little information available on them, particularly concerning their effect on the environment.

"REACH is based on the idea that industry itself is best placed to ensure that the chemicals it manufactures or puts on the market do not adversely affect human health or the environment." [ii]

REACH places the responsibility for the control and safe use of substances firmly on the shoulders of industry. It is up to industry to prove that their substances are safe and adequately controlled.

Manufacturers and Importers must register all substances which they manufacture, import or supply within the EU in quantities of 1 ton per year or more. This applies to substances:

- on their own;
- as intermediates;
- in preparations (e.g. inks);
- in articles (e.g. scented candles), where there is an intended or foreseeable release during normal use.

Registration involves preparing a Technical Dossier (TD) and Chemical Safety Report (CSR) covering information on properties, uses, hazards, exposure scenarios and risk control measures. If a substance is not registered it basically cannot be placed on the market within the EU (applicable on regular substances with a volume of >1000 t/a).

*REACH, Regulation (EC) No 1907/2006, Art. 5:*

# "NO DATA, NO MARKET"

If a manufacturer or importer does not register the substances it manufactures or imports, then there will be no data available and so it will not be able to manufacture or import these substances legally. The law promises that any chemicals which are not registered may not be sold. Only after all data is gathered and submitted can these chemicals once again be sold in Europe. Principle: "No data, no market".

The implementation timeframe is:

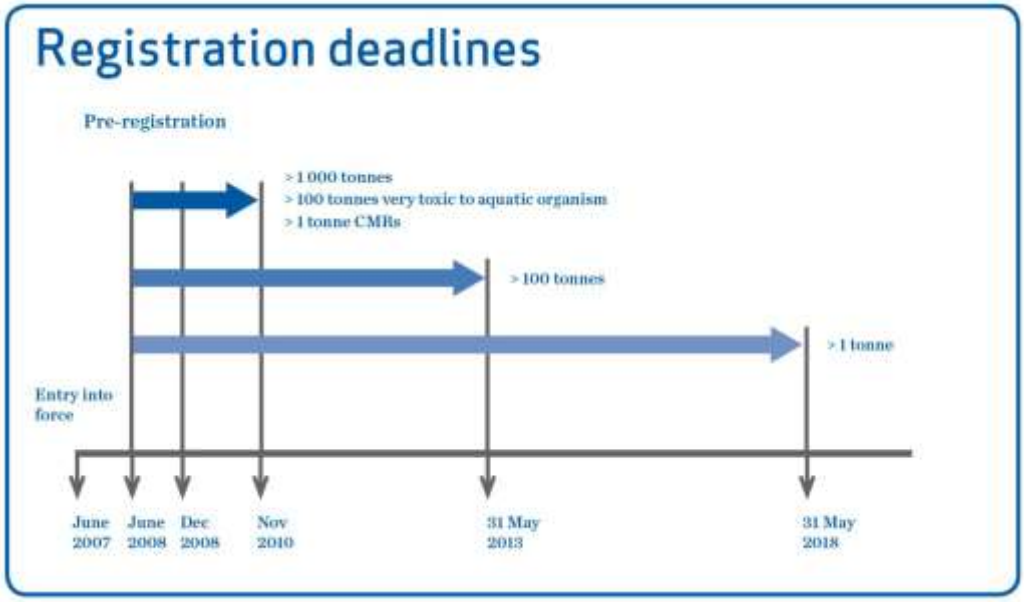



Figure 1: Registration deadlines under REACH [iii]

## 2. LIMITATIONS TO THE EXEMPTIONS FOR FOOD INDUSTRY

The REACH regulation does not only affect chemical manufacturers and importers, but also imposes, for the first time, far-reaching requirements on virtually all producers using substances in their goods and manufacturing processes. The entire supply chain will have to examine and disclose the properties of the substances they use, and ensure that the safety in their specific downstream use is satisfied.

Substances that are intended to be used in food and feedingstuffs are exempted from the REACH regulation's requirements on registration, evaluation, authorization, and downstream use of substances. This is because the regulation exempts from these requirements substances "used in food or feedingstuffs," and the European Food Regulation defines food as "any substance or product, whether processed, partially processed or unprocessed, *intended to be, or reasonably expected to be* ingested by humans." [iv] Similarly, feed is defined as "any substance or product, including additives, whether processed or partially processed or unprocessed, *intended to be used* for oral feeding to animals." [v] Thus, imported foods and feedingstuffs and their ingredients would be exempted from the REACH.

In addition to those substances which are totally exempt from REACH[vi], there are a number of substances which are exempt from only certain aspects of REACH. This is often because they are used in products which fall under the scope of more specific legislation. These are listed below together with the relevant article of the REACH text and the part of REACH from which they are exempt.

1. Substances contained within products falling into scope of the following European Directives and Regulations are exempted from the following parts of REACH: Title II (Registration); Title V (Downstream Users); Title VI (Evaluation); Title VII (Authorisation)

- Medicinal products [Article 2(5)(a)];
- for human use within the scope of Directive 2001/83/EC;
- for veterinary use within the scope of Regulation (EC) No 726/2004, Directive 2001/82/EC.
- **Food and Feedingstuffs in accordance with Regulation (EC) No 178/2002 [Article 2(5)(b)]; including use**
- **as a food additive in foodstuffs within the scope of Directive 89/107/EEC;**
- as a flavouring in foodstuffs within the scope of Directive 88/388/EEC and Directive 1999/217/EC drawn up in application of Regulation (EC) No 2232/96;
- as an additive in feeding stuffs within scope of Regulation (EC) No 1831/2003;
- in animal nutrition within the scope of Directive 82/471/EEC.

2. Substances contained within products in the **finished state**, intended for the **end user**, falling into scope of the following European Directives and Regulations are exempted from the following Parts of REACH: Title IV (Information in the supply chain) [Article 2(6)]

- Medicinal products (as per the bullet point above);
- Cosmetic products as defined in Directive 76/768/EEC;
- Medical devices which are invasive or used in direct physical contact with the human body in so far as Community measures lay down provisions for the classification and labelling of dangerous substances and preparations which ensure the same level of information provision and protection as Directive 1999/45/EC;
- **Food and Feedingstuffs (as per the bullet point above).**

## 2.1 NOT EXEMPTED FOR FOOD INDUSTRY

To better understand which aspects are not exempted within the food manufacturing process one could start by looking at the ECHA's FAQ ID 182[vii] answer:

*According to Article 1(5)(e) of CLP, the CLP Regulation does not apply to food and feeding stuffs, as defined in Regulation (EC) No 178/2002 (Food Safety Regulation), and which are in the finished state intended for the final user. The CLP Regulation does not define the term "final user", but Regulation (EC) No 178/2002 defines "final consumer" as "the ultimate consumer of a foodstuff who will not use the food as part of any food business operation or activity". The same concept can be applied in the context of CLP. This also applies to the use of a substance or a mixture as a food additive in foodstuffs within the scope of Directive 89/107/EEC,*

- *as a flavouring in foodstuffs within the scope of Directive 88/388/EEC and Decision 1999/217/EC,*
- *as an additive in feeding stuffs within the scope of Regulation (EC) No 1831/2003 or*
- *in animal nutrition within the scope of Directive 82/471/EEC.*

*Since Article 1(5)(e) of CLP only refers to food or feeding stuffs in the **final state** intended for the **final user** substances or mixtures used in food or feeding stuffs at any stage of production are not exempt from CLP and therefore must be classified, packaged, labelled and notified. For instance, the CLP Regulation applies to the manufacturer/supplier of a food additive (e.g. preservatives) who supplies the substance to another company that uses it in the production of food. In such a case, the chemical substance in the form in which it is supplied should not be regarded as a product being in the finished state intended for the final user, and the exemption stated in Art. 1(5)(e) CLP is not applicable (see also FAQ ID=179).*The

This same reasoning is applicable to the REACH exemptions since it refers to the same articles.

In line with this answer FEDIMA (Federation of European Union Manufacturers and Suppliers of Ingredients to the Bakery, Confectionery and Patisserie Industries) states in its statement on the consequences of REACH and CLP[viii] that food mixes or bakery ingredients used by industrial or craftbakers "business to business" that meet the criteria for classification of hazardous substances are subject to REACH and CLP legislation.

The food industry interprets REACH Regulation's exemptions as not applying to processing aids and (chemical) intermediates used in the EU manufacture of food and feed but that are not intended themselves as food or feed ingredients.

Processing aids are defined as "any substance not consumed as a food ingredient by itself, intentionally used in the processing of raw materials, foods or their ingredients, to fulfil a certain technological purpose during treatment or processing and which may result in the unintentional but technically unavoidable presence of residues of the substance or its derivatives in the final product, provided that these residues do not present any health risks and do not have any technological effect on the finished product." See Footnote 1 of Council Directive 89/107 on food additives authorized for use in foodstuffs intended for human consumption O.J. [1989] L40/27. This definition could be revised during the adoption of the Commission Proposal for a Regulation on Food Additives COM (2006) 428 final (Brussels, 28 July 2006).

In REACH terms, an intermediate is "a substance that is manufactured for and consumed in or used for chemical processing in order to be transformed into another substance."

Both processing aids and intermediates may be subject to the full scope of REACH. Reagents used in the modification of starch fall in the same line of legislation and are therefore also **not exempted from REACH**. These obligations may include the need to register substances manufactured in, or imported into, the EU in quantities of one ton or more per manufacturer/importer per year; and authorization in the case of substances of very high concern.

Processing aids and intermediates, however, could be exempted from the registration requirement if they are (i) natural, (ii) not chemically modified, and (iii) not classified as "dangerous". Certain substances listed in Annex IV to the Regulation, which are common use in the manufacturing of food and feedingstuffs, such as pure sucrose, sunflower oil, corn oil, and D-mannitol, are also exempted from the requirement of registration. These substances could, nevertheless, still be subject to other REACH requirements, such as authorization and restrictions.

## 2.2 REACH HELPDESK POINT OF VIEW

The Dutch REACH helpdesk confirmed that the reaction products of acetic anhydride and adipic acid need to be REACH registered. AD International also contacted the REACH helpdesks of other EU member states. These helpdesks confirmed that the helpdesks in the EU Member States (EU MS) cooperate to give consistent advice about REACH across Europe, so there should not be any difference in the interpretation of different helpdesks.

With regards to the interpretation of the food exemption the Dutch helpdesk recommended AD International to contact the Dutch NVWA, which is the competent authority in the Netherlands for food law regulations.

## 2.3 FOOD LAW REGULATION, COMPETENT AUTHORITIES POINT OF VIEW

**Food law regulation European responses**

The response from the NVWA (Netherlands) with regards to the question if processing aids are covered or not covered by the Food Safety regulations:

*"The NVWA distinguishes 2 kinds of processing aids: Processing aids which are considered as food(stuff), for instance additives and processing aids which are not considered to be food(stuff), for instance a kind of silica earth. The first group of processing aids are substances which are not at first marketed as processing aids but as 'food(stuff)', for instance an additive. Solely by using this substance during processing of food it becomes a processing aid. The substance itself is however considered as food and should comply with the Food Legislation.The second group of processing aids are not food(stuffs) but are marketed to come into contact with food to carry out a certain technological function during processing. These kind of processing aids should be registered under REACH."*

Because each EU MS has its own competent authority for food law regulations AD International contacted several other EU MS to come up with a uniform interpretation of this matter. To quote several of their responses:

**Ministerium für ein levenswertes österreich (Austria):**

*"The registered substance is a reagent for the modification of starch. The manufacturer/importer has the obligation to register under REACH as the substance is not used in (or as a part of) food or feeding stuff. The substance is rather used in a modification step of starch, therefore the exemption of Art. 2(5)b REACH cannot be applied. We note that this interpretation is solely based on the provisions of the REACH regulation."*

**The Danish Veterinary and Food Administration/DVFA (Denmark):**

*"The general food law does not cover (h) residues and contaminants. The DVFA consider processing aids to be covered by this exemption. So processing aids as substances are not covered by the general food law. This is a Danish interpretation of the rules."*

Based on the responses of both the REACH helpdesk and the competent food law regulation authorities the conclusion can be drawn that the need for REACH registration of the reaction products of acetic anhydride and adipic acid is valid and supported.

## CONCLUSION FOR STARCH MANUFACTURING

As such both the starch starting material and the modified starch end product are exempted under one of more of the previous mentioned regulations and directives, but the reagents used in the modification are not exempted, as these exemptions do not cover the intermediate process of modification itself. This reasoning is supported by the European REACH helpdesks and national food law regulation competent authorities.

In the next chapters the use of adipic acid and acetic anhydride functional materials and its reaction products will be further elaborated on, as well as the need for registration of the reaction substance under REACH.

## 3. USE OF ADIPIC ACID ANHYDRIDE FUNCTIONAL MATERIALS IN STARCH MODIFICATION

Acetic anhydride and adipic acid are used in the treatment of starches to resist high temperatures. The main used of these modified starches is the use as stabilizer or thickener. The resulting modified starches are listed as food additive in the EC as additive E1422.

Cross-linking is one of the most common types of chemical modifications because the reaction has a strong effect on the viscosity profile of a starch. Cross-bonded starches are used by industry because they have a relatively constant viscosity during heating and cooling. Starches crossbond intra- and intermoleculary due to the reaction of hydroxide groups, increasing the molecular weight.[ix] The mixed adipic and acetic anhydride reagent also creates ester linkages substituted with acetyl groups.

Technically these reactions are well known and well described. Actually as early as in 1960, O. Wurzburg obtained US patent 2.935.510 titled "Preparation of starch derivatives"[x], describing the use of mixed adipic/acetic anhydrides as esterification reagent in thee modification of among others tapioca, potato and maize starches.

Starch has been an inexhaustible subject of research for many decades. It is an inexpensive, readily-available material with extensive application in the food and processing industry. Researchers are continually trying to improve its properties by different modification procedures and expand its application. What is mostly applied in this view are their chemical modifications, among which organic acids have recently drawn the greatest attention, particularly with respect to the application of starch in the food industry. Namely, organic acids naturally occur in many edible plants and many of them are generally recognized as safe (GRAS), which make them ideal modification agents for starch intended for the food industry. Research on these modifications is still taking place for example by Đurđica Ačkar et.al.[xi]

Adipic acid/acetic anhydride modified starches are often favored because of the high paste clarity, improved stability and high viscosity values; although the lower water solubility at high conversion rates can lead to technical challenges.

Adipic acid is a commonly used reagent for starch modification. Since it has two carboxylic groups, it can produce cross-linked starch, as well as mono-substituted derivatives. The reaction is conducted in a water suspension, in alkali conditions, by the drop-wise addition of acetic anhydride/adipic acid mixture.

By mixing acetic anhydride and adipic acid, Adipic acid, di-anhydride with bis(acetic acid) can be formed. This anhydride reacts with starch producing a distarch adipate and acetic acid (Figure 3). At pH 8.0 the reaction is fast, but the reagent has to be slowly added with the pH maintenance.

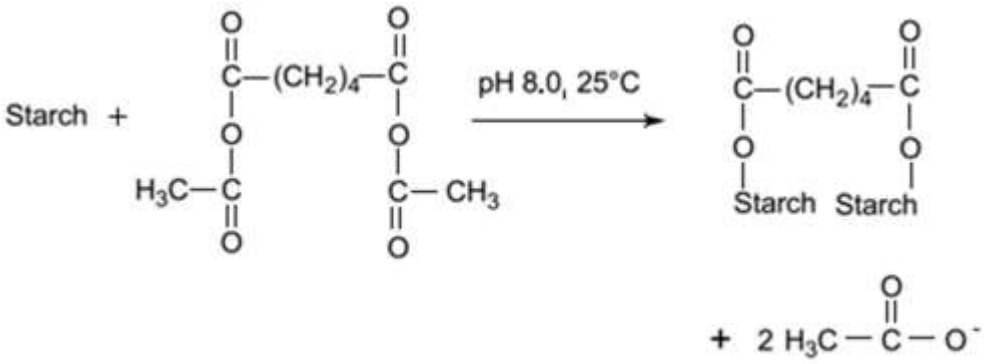



Figure 2: Cross-linking of starch with adipate [ii]

Distarch adipates show enhanced stability during shearing at high temperatures, at low pH, and in freeze-thaw cycles, which is a clear advantage in the food processing industry compared to native starches.

# 4. REACH: REACTION PRODUCTS OF ACETIC ANHYDRIDE AND ADIPIC ACID

Following the conclusions from chapter 2 the substance “Reaction products of acetic anhydride and adipic acid” is subject to REACH. In this chapter an in-depth analysis of the process of creation and the resulting substance will be described.

After looking more closely at the available literature and additional testing using IR spectral analyses AD International BV has come to the conclusion that the product supplied is not a mixture of acetic anhydride and adipic acid. The results clearly show that the resulting product is a new substance and as such is subject to the registration process as described in the REACH Regulation.

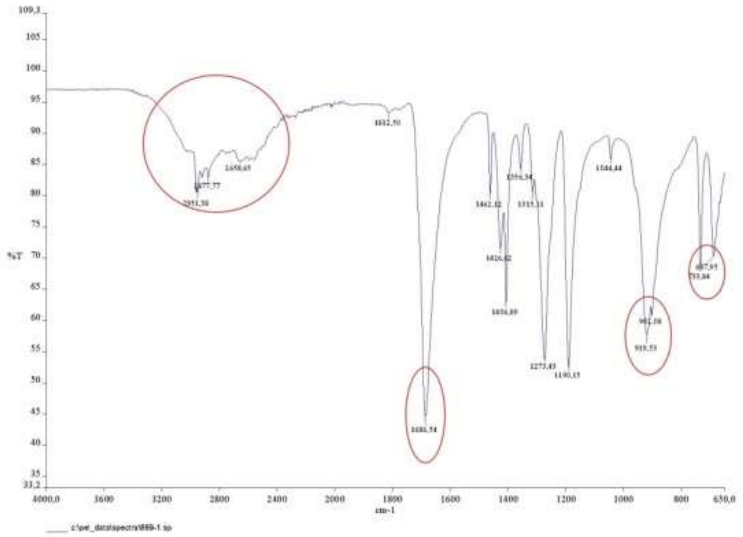


Figure 3:
Reference adipic acid

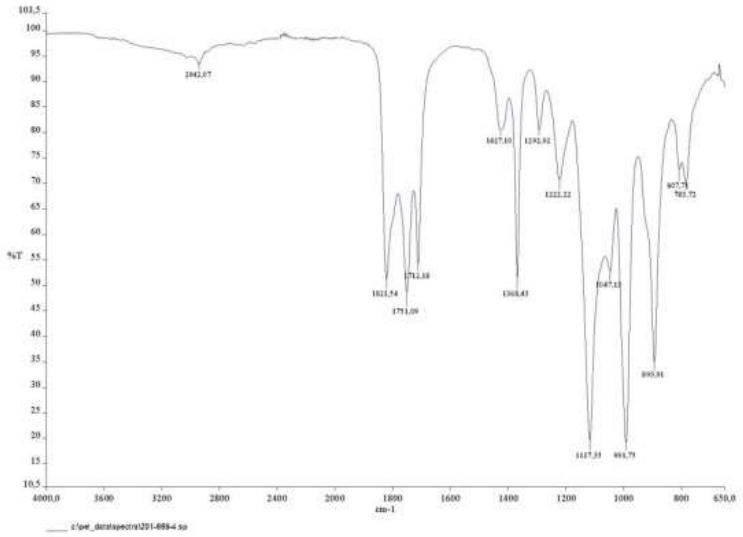


Figure 4:
The reaction mixture in acetic anhydride

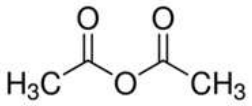
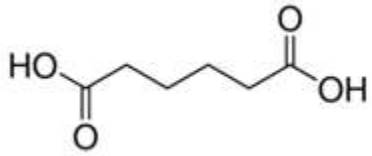
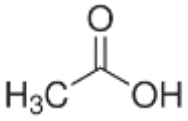
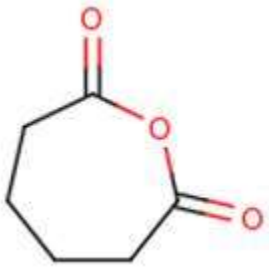
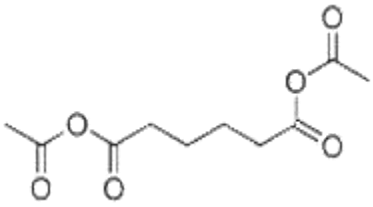
The spectrum for adipic acid shows significant absorption at the characteristic frequencies, which are no longer present in the spectrum of the reaction mixture, supporting the claim for 100% conversion of the adipic acid to the mixed adipic anhydrides.

A spectral analysis of possible structures giving these absorptions was made using the reference tables as published by Silverstein e.al, Spectrometric Identification of organic compounds. 7th edition, pg 119-126.

| **Wavelength (cm-1)** | **Structures** |
|---|---|
| | |
| 2942 | Dimers of carboxylic acids<br>Alkanes |
| 1821 | Anhydrides |
| 1752 | Acetates |
| 1712 | Dimers of carboxylic acids |
| 1292 | Dimers of carboxylic acids<br>Cyclic anhydrides |

The peak ratio between the 1292 and other absorption peaks is such that the formation of dimers, trimers and a cyclic anhydride are more than likely next to the main constituent adipic-acid-dianhydride. The relative intensity of the peaks however suggests that the adipic acid is for over 90% converted to the main component.

Table 1: substances formed in the reaction mixture

| CAS | EINECS | Material | Structure |
|---|---|---|---|
| 108-24-7 | 203-564-8 | Acetic anhydride |  |
| 124-04-9 | 204-673-3 | Adipic acid |  |
| 64-19-7 | 200-580-7 | Acetic acid |  |
| 2035-75-8 | 218-001-1 | Adipic anhydride |  |
| 38478-77-2 | 253-964-1 | Adipic acid, di-anhydride with bis(acetic acid) |  |

# 5. REACH INFORMATION

AD International BV has been working on the REACH registration of this reaction products of acetic anhydride and adipic acid and received the registration number in 2016.

| | |
|---|---|
| **Registration number:** | **01-2120115217-67-0000** |
| **EC number:** | **943-366-5** |
| **Description:** | **Reaction products of acetic anhydride and adipic acid** |

## 5.1 AD INTERNATIONAL BV AND REACH KNOWLEDGE

AD International BV has followed the debates and progress of REACH from the early stages and has more than seven years of knowledge to ensure successful REACH implementation. AD International BV supports the objectives of REACH that comply with its Safety, Health and Environmental Sustainability Policy.

For establishing the REACH registration of the reaction products of acetic anhydride and adipic acid AD International BV has been collaborating closely with international independent consultancy firm REACHLaw.

REACHLaw provides chemical regulatory compliance and product safety solutions globally. REACHLaw has its headquarter in Finland and offices in Belgium, Turkey and India. REACHLaw has vast experience in taking companies through the different phases of the REACH registration process including SIEF and Consortium. It provides resources and expertise for the hazard assessment, exposure assessment and risk characterization when needed.

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## REFERENCES

[i] A copy of the Regulation is available at:
http://eur-ex.europa.eu/LexUriServ/site/en/oj/2007/l_136/l_13620070529en00030280.pdf

[ii] Reach in Brief, European Commission, Feb 2006

[iii] ECHA information: http://echa.europa.eu/documents/10162/13632/nutshell_guidance_registration_en.pdf

[iv] Article 2(1) of Regulation (EC) No. 178/2002 of the European Parliament and of the Council laying down the general principles and requirements of food law, establishing the European Food Safety Authority and laying down procedures in matters of food safety O.J [2002] L31/1.

[v] Article Article 3(1)(4) of Regulation (EC) No. 178/2002 of the European Parliament and of the Council laying down the general principles and requirements of food law, establishing the European Food Safety Authority and laying down procedures in matters of food safety O.J [2002] L31/1.

[vi] ECHA, Am I exempt, http://echa.europa.eu/nl/support/getting-started/am-i-exempt

[vii] Questions and answers, ECHA:
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[viii] FEDIMA, Statement on the consequences of REACH and CLP Regulations on bakery ingredients, September 2013

[ix] Cross-Bonded Starches, Cereal Grains: Properties, Processing, and Nutritional Attributes
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[x] US Patent 2,935,510 (May 1960), PREPARATION OF STARCH DERIVATIVES, Otto B. Wurzburg, Whitehouse Station, NJ., assignor to National Starch and Chemical Corporation, Application June 6, 1958, Patent US2935510

[xi] Starch Modification by Organic Acids and Their Derivatives: A Review, Đurđica Ačkar, Jurislav Babić, Antun Jozinović, Borislav Miličević, Stela Jokić, Radoslav Miličević, Marija Rajič 1,† and Drago Šubarić. Molecules 2015, 20, 19554-19570; doi:10.3390/molecules201019554, www.mdpi.com/journal/molecules