Hydroquinone - Past, Present, Future

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Abstract

Up to now almost all b/w developers contain hydroquinone as the main developing agent. The photochemical industry is extending its range of products with b/w developers, based on sodium isoascorbate. However, while isoascorbate may be perceived as an available alternative to hydroquinone, there are a number of economic and technical drawbacks associated with using isoasacobate.

Introduction[1]

Hydroquinone or 1,4-dihydroxybenzene (CAS registry number 123-31-9), discovered as being a powerful photographic developing agent in 1880 by Sir William Abney de Wiveleslie (1843-1920), is still widely used as a developer in black/white photography and related graphic arts and for medical and industrial X-ray films. Almost all b/w developers contain hydroquinone as the main developing agent, in many cases supported by secondary developing agents like phenidone or metol (elon). Other industrial applications for hydroquinone are as antioxidants and as polymerisation inhibitors. The worldwide consumption is around 30,000 tonnes/year, of which roughly 50% is used in photography, 40% in antioxidants and 10% for polymerisation inhibitors.

Hydroquinone, a white crystalline powder with a melting point of 173-174 °C , was obtained for the first time by Pelletier and Caventou in 1820 by the dry destillation of quinic acid. In 1844 Wöhler determined its stucture and baptisted it hydroquinone. Hydroquinone is soluble in water (70 g/l at 25 °C). It is a reducing agent which is reversibly oxidized to its semiquinone and quinone.

In nature hydroquinone occurs in several plants in the form of a β-D-glucopyranoside called arbutin, by hydrolysis hydroquinone is formed. Arbutin can be found in the leaves of many plants, among others those of certain berries (blueberry, cranberry, bearberry, cowberry), as well as in the bark of the pear tree. Hydroquinone can be found in coffee beans, in tea prepared from leaves of several berries, in red wine and in broccoli. Hydroquinone has been found in cigarette smoke (about 0.1 mg/cigarette). Arbutin is present in a variety of food stuffs: wheat germ, pear skin, diet cola. The quantity of hydroquinone consumed after having a normal breakfast of 1 serving of wheat cereal, 1 slice of whole wheatbread and 1 mug of coffee is estimated to be 0.2 mg. Low concentrations of hydroquinone have been detected in the urine and plasma of humans with no occupational or other exposure to hydroquinone.[2]

Hydroquinone can be secreted by grasshoppers and caterpillars.

In the process of composting hydroquinone derivatives play an important role (soil humic acids).[3]

Furthermore hydroquinone can be found in some cosmetic creams and medical skin preparations as a depigmenting agent to lighten small areas of hyperpigmented skin. In the EU a maximum of 2 percent of hydroquinone in cosmetics is allowed.
The hydroquinone level in photographic black/white developers varies in general between 0.3 and 3 percent, depending on the field of application.

One of the commercial ways of synthesis of hydroquinone starts with the oxidation of aniline sulfate to quinone by manganese dioxyde or chromic acid, followed by the reduction by iron dust in water to hydroquinone. Hydroquinone is also manufactured by the alkylation of benzene with propylene to produce a mixture of diisopropylbenzene isomers. The para-isomer is isolated and oxidized with oxygen to produce the corresponding dihydroperoxide, which is treated with sulfuric acid to produce acetone and hydroquinone. Several other routes of synthesis are also described.

Hydroquinone: toxicology

For more than a century hydroquinone has been considered to be a safe compound to work with. It has a relatively low toxicity. With a LD50 (oral-rat) value of 320 mg/kg body weigth the pure substance is classified as being harmful to the health, but in practical photographic use no toxicity warnings are needed because of the low concentrations applied. The only warning used by the European photographic industry is an irritant warning as there are a couple of cases in the medical literature stating that users showed an allergic skin reaction because of their contacts with photographic developing solutions.

Hydroquinone: carcinogenity ?

Only recently some articles have been published in which reference is made to the suspected carcinogenic properties of hydroquinone, obviously resulting in fear of the photographic workers, questions by the workers unions as well as a reconsideration of OEL's (occupational exposure limits) and labelling systems in Germany, The Netherlands, Scandinavian countries and the European Union.
It is without saying that these articles have been carefully studied by the photochemical industry, discussed in the Health, Safety and Environmental Meetings of the CEFIC European Photochemical Industry Sector Group and discussed with the main manufacturers of hydroquinone as well.

The conclusion of all consulted toxicologists is that indeed hydroquinone may cause cancer in some types of rats (but not in all rats) but that this cancer is not expected to occur in human beings because of the differences in metabolism between human beings and that type of rats.

An epidemiology study of 879 employees manufacturing hydroquinone has shown that the incidence of cancer and early death were lower among hydroquinone manufacturing personnel than in the general population and in comparison to other manufacturing employees.[4]

The recent Scandinavian publication on the higher incidence of skin cancer among lithographers and suggested to be caused by hydroquinone exposure is far from conclusive and most likely wrong, as it is a well-known fact that hydroquinone on the contrary might inhibit or destroy melanoma cells.[5-6]

Hydroquinone: regulatory status

(a) Europe: In the Annex I to the EU Classification, Packaging, and Labelling of Dangerous Substances Directive 67/548/EEC the classification of hydroquinone is Xn (harmful), R 20/22 (Harmful by inhalation and if swallowed.). Currently hydroquinone is on the agenda of the Expert Group of the Technical Progress Committee, the expectation is that the committee might decide by the end of 1997 to add to the classification the carcinogenity category 3 (R40: Possible risks of irreversible effects.). If this happens, it will take another one to two years before this modified classification will be implemented in the national legislations.

(b) Germany: MAK Commission. In 1994 the German Treshold Limit Value Committee (MAK-Kommission der Senatskommission der Deutschen Forschungsgemeinschaft zur Prüfung gesundheitsschädlicher Arbeitsstoffe) has classified hydroquinone as a carcinogenic compound in animal tests (class IIIA2) as well as a mutagenic compound (lowest category). The German Working Group for Dangerous Substances (AGS = Arbeitskreis für Gefahrstoffe) only partly accepted this classification; its classification is category 3b, compounds that are suspected carcinogenic compounds for humans, but for which not enough data are available yet. The results of the animal tests are not convincing enough for a more severe classification. This classification is for Germany legally binding. For example, the new German TRGS 900 and 905 (TRGS = Technische Regeln Gefahrstoffe = technical regulations for dangerous substances) already have implemented this AGS-decision. The practical meaning of this classification is that in Germany Safety Data Sheets should contain the category 3b warnings, but the labelling of the products remains unchanged, as the labelling of dangerous substances and preparations has to follow the European Directives.

(c) Germany: WGK Classification. In the last months of 1996 the German KBwS Commission (KBwS = Kommission Bewertung wassergefährdender Stoffe = Commission for the classification of water endangering compounds) has proposed to reclassify hydroquinone from WGK (water endangering class) 2 into 3 (from water endangering into strongly water endangering). This reclassification proposal is partly based on the MAK Committee work, partly on the fact that hydroquinone is quite toxic to aquatic species (LC50 fathead minnow, 96 h. < 1 mg/l). The German Fachverband der Photochemischen Industrie is not in agreement with this reclassification, as according to their scientists the good biodegradability of hydroquinone has not been sufficiently taken into account. Furthermore, the industry has requested the KBwS to postpone the decision for reclassification until the EU has published its revised Annex I.

(d) The Netherlands: MAC Commission. The Dutch expert committee on occupational standards, a commitee of the Health Council of the Netherlands (Gezondheidsraad) has published a draft-report on "Health based recommended occupational exposure limit for p-benzoquinone and hydroquinone".[7] According to EU criteria for the classification of carcinogenic compounds the committee classifies both compounds in Group 3A (the compounds are well investigated, but the evidence of a carcinogenic effect is insufficient to classify these compounds as probably carcinogenic to humans. The compounds are considered as suspected carcinogens.).

To prevent myelotoxic effects, the committee recommends to limit exposure to a concentration of 0.28 mg/m^3 (0.06 ppm) for p-benzoquinone and hydroquinone together. The committee recommends to assign a skin notation to both compounds.

(e) The American Conference of Governmental Industrial Hygienists (ACGIH) has found no reasons to change the Threshold Limit Value (TLV) of 2 mg/m^3 (time-weighted average) as well as the classification in Class A3:

carcinogenic for animals at high doses and by route not related to human exposure.

Developers: low exposure

In the opinion of the photochemical producers it is safe to work with hydroquinone-containing developers, not only because of the relatively low toxicity of hydroquinone, but also because of the low exposure risk for the workers. Hydroquinone in alkaline developer solutions is in an ionized form and will not evaporate. If one is buying the chemistry in a powder form, it is a good practice to be careful in avoiding dust when preparing the solutions, and there are good equipment and systems available to avoid any dust formation.

Hydroquinone: alternative

In some cases it is possible to use ascorbates as an alternative for hydroquinone. The chemical name of Vitamin C is ascorbic acid, one of its synthetic non-biological active stereo-isomer is called isoascorbic acid or erythorbic acid (CAS registry number 89-65-6). The sodium salts of both acids work well as developing agents. However, because of the difference in molecular masses between hydroquinone and these salts (hydroquinone 110.11, isoascorbic acid 176.14), the double quantity is required in order to get a comparable performance. The safety aspects of isoascorbates are excellent, as these compounds are allowed to be used as an anti-oxidant in foodstuffs. The developing properties of ascorbic acid were already described in the photographic literature by Öhle in 1932, but only in recent years the first practical applications are appearing on the market.

The photochemical industry has been successful in formulating isoascorbate-based developers for a couple of applications with properties that could be compared to a hydroquinone-based developer. These R&D-projects have been quite tough as it became very clear that isoascorbates are not just a plug-in for hydroquinone. All parts of the developer had to be readjusted and still the performances are not fully the same, although this will be hardly noticeable in practice. Up to now it has not been possible to formulate hydroquinone-free developers for all applications.

The isoascorbate developers are more expensive compared to the hydroquinone ones, as more developing agent (on weigth basis) is needed. Because of the higher amounts of developing agent needed more waste is produced. Furthermore the price of isoascorbate salts is almost double that of hydroquinone.

The biodegradation value of isoascorbic acid, obtained using the 1992 version of the OECD Guideline 301E, is 52 percent DOC removal (28 d.), that of hydroquinone under the same conditions is 61 percent.[8] The limit value for a substance being "readily biodegradable" under these conditions, is $\geq$ 70 percent. In the literature higher biodegradability values for hydroquinone (up to 81 percent) can be found. Some of these studies were performed with pre-adapted micro-organisms or acclimated micro-organisms in dynamic tests. According to the OECD Screening Test 301E a pre-adaptation of the micro-organisms to the test substances is not allowed.

The German WGK-classification of isoascorbic acid as well as its sodium salt is 0 (in general not water-endangering).

At the Photokina 1996, the World Fair for Imaging in Cologne, Germany two companies were introducing hydroquinone-free developers for amateur use:

Kodak presented the two part powder developer Xtol for processing black-and-white films.[9] According to the Safety Data Sheet the composition of the working strength solution is 85-95% water, 5-10% sodium sulfite, 1-5% sodium isoascorbate, < 1% sodium metaborate, tetrahydrate and < 1% diethylenetrisodiumpentaacetic acid sodium salt; pH 8.2.

Agfa presented a new hydroquinone-free liquid concentrate developer Neutol Plus for the processing of black-and-white papers. Dilution: 1+4.

At the Imprinta '97 pre-press fair in Düsseldorf (Germany) Agfa presented the first hydroquinone-free graphic arts developer: the AgfaSave Rapid Access Processing System, using isoascorbate as the developing agent.

Also DuPont has a hydroquinone-free developer: The DuPont DuCare Recycled Developer. This developer contains among others isoascorbic acid, potassium sulfite, sodium sulfite, potassium hydroxide and water.

It goes without saying that other companies are about to introduce their hydroquinone-free developers too.

Hydroquinone developers: the future

Photochemicals producers consider working with hydroquinone-based developers as safe. The industry has a long history of safe use of these developers and the recently completed human epidemiology study provides further documentation of the safety of these products. While, non-hydroquinone developers have been on the market for several years and recent additions have been made to the list of available non-hydroquinone developers, many users of black/white developers will continue to want to use hydroquinone-baed developers because of their superior technical performance and lower cost. Where the technical drawbacks of using a non-hydroquinone developer can be overcome, the photochemical industry has offered its customers alternative products so that the customer is able to make the choise between which type of developer is used. Whichever choice the customer makes, it is the photochemical industry's goal to provide safe and effective developers which meet customer needs.

The photochemical industry is of the opinion that it is - by introducing this new line of products in this way - fully respecting the principles of the "Responsible Care" programme of the chemical industry world-wide.

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