

ALIEN PROPERTY CUSTODIAN

PREPARATION OF PHTHALOCYANINES

Hans Hoyer, Frankfurt A. M., Hans Colombara, and Berthold Bienert, Leverkusen-L. G. Werk, Germany; vested in the Alien Property Custodian

No Drawing. Application filed July 24, 1941

The present invention relates to improvements in the preparation of phthalocyanines according to the so-called urea process.

It is known that phthalocyanines can be prepared by heating aromatic o-dicarboxylic acids or the corresponding anhydrides, ammonium salts, amides or imides with urea or heat-decomposition products thereof (other than ammonium) and a metal salt, for instance a copper salt, to a higher temperature. In many cases, this process is accompanied by an undesirable foaming of the melt. Thereby the disadvantage is involved that, owing to the high isolating capacity of foams, the reaction mixture can not be completely kept at the necessary reaction temperature. In consequence thereof, such processes are liable to yield a relatively low amount of the desired dyestuff.

It is the object of the present invention to do away with these advantages and to develop a modified urea process which allows one to prevent the formation of foams and to increase the yield of the desired phthalocyanine dyestuffs. Other objects of our invention will be apparent from the following description and claims.

It has been found that the disadvantages as explained above can be overcome by effecting the said process in the presence of such aromatic carboxylic acids or sulfonic acids or the amides thereof as are not capable of being converted into phthalocyanines. These auxiliary agents are effective only, as far as our hitherto experiments have shown, in the case of such phthalocyanine forming starting materials (i. e. aromatic dicarboxylic acids, amides, imides thereof etc.) as contain sulfonic acid groups or carboxylic acid groups in addition to those carboxylic acid groups which take part in the phthalocyanine forming reaction. Suitable auxiliary agents of the character described are, for instance, benzoic acid, benzene sulfonic acid, nuclear substitution products thereof and the amides of the said materials. Such auxiliary agents of the character described are preferred as are soluble in water either per se or in form of their alkali metal salts as such properties allow one to remove the said auxiliary agents from the melt after reaction by contacting the same with water or with a caustic soda lye. Depending on the nature of the starting materials and on the reaction conditions which are decisive for the more or less pronounced tendency of forming foams, the amount of the auxiliary agents may vary within wide limits. In general, an amount of about 20-30 per cent of the said auxiliary agents (calculated on the amount of the urea) is sufficient to exert the desired effect.

Generally, the efficacy of the said auxiliary agents is the better the higher the amount and the weight of the substituents which are present in the aromatic o-dicarboxylic acids. Benzamide has proved to be best suitable for the purpose in question.

Our invention is furthermore illustrated by the following examples, without, however, being restricted thereto:

Example 1

Into a melt of 70 g of urea there is added at a temperature of 140-145° C a mixture of

	Grams
Diphenyl-2.4.5-tricarboxylic acid.....	100
Benzoic acid.....	20
Copper chloride or an equimolecular amount of cobalt or nickel chloride.....	20

Thereupon, 0.6 g of ammonium molybdate are added and the melt is slowly heated to a temperature of 160-165° C, whereat a mixture of 100 g of urea and 20 g of benzoic acid is slowly added in such proportions that the melt never loses the capability of being agitated. The working up is effected by diluting the melt with water, rendering the same alkaline, removing the separated copper oxide and precipitating the phthalocyanine tetraphenyl tetracarboxylic acid by the addition of a mineral acid.

A similar result is achieved when using toluic or naphthoic acid instead of benzoic acid.

Example 2

Into a melt of 2.35 g of urea there is added while stirring at a temperature of 162-163° C a mixture of

	Grams
Urea	11.4
Potassium-4-sulfophthalate	11.4
Crystallized copper chloride.....	1.7
Ammonium molybdate.....	0.342
Benzoic acid	2.75

The melt is kept for about 4 hours at a temperature of 162-163° C, whereupon further 2.35 g of urea are added. After cooling down to about 100° C the melt is diluted with water, rendered slightly alkaline by means of caustic soda whereupon the so formed dyestuff is precipitated by the addition of sodium chloride. By redissolving the same from diluted hydrochloric acid there can be removed any traces of copper salts which might still be present therein.

The yield of dyestuff is 8 per cent higher than when working without benzoic acid.

Example 3

Into a melt of 7.5 g of urea there is added while stirring at a temperature of 162-163° C a mixture of

	Grams
Urea	15.0
Potassium 5 - benzoylamino-4-sulfophthalate	15.0
Crystallized copper chloride.....	1.58
Ammonium molybdate.....	0.45
Benzoic acid or m-chlorobenzoic acid, benzamide, N-monomethylbenzamide, p-toluene sulfonic acid or p-toluene sulfamide	6.75

The melt is kept for about 4 hours at a temperature of 162-163° C, whereat further 7.5 g of urea are added. A good yield of the corresponding copper phthalocyanine is obtained, whereat no foaming of the melt is observed.

Example 4

Into a melt of 5.2 g of urea there is added while stirring at a temperature of 162-163° C a mixture of

	Grams
Urea	21.9
Potassium-5-(2-chlorobenzoylamino)-4-sulfophthalate	21.9
Crystallized copper chloride.....	2.15
Benzoic acid.....	6.5
Ammonium molybdate.....	0.65

The melt is kept for about 4 hours at a temperature of 162-163° C, whereat further 5.2 g of urea are added. The melt does not foam, the corresponding copper phthalocyanine being formed in a yield of 67%, whereas the yield is about 38% in the case of working without benzoic acid.

Example 5

Into a melt of 3.9 g of urea there is added while stirring at a temperature of 180° C a mixture of

	Grams
Urea	7.8
Potassium-5-(2-chlorobenzoylamino)-4-sulfophthalate	7.8
15 Copper chloride or of an equimolecular amount of nickel chloride or cobalt chloride	0.765
Ammonium molybdate.....	0.235
p-Methoxybenzoic acid	2.34

20 The melt is kept for about 4 hours at a temperature of 180° C, whereat further 3.9 g of urea are added. The sodium 5.5'.5''.5'''-(tetra-4-methoxybenzoylamino) - copper - phthalocyanine - 4.4'.4''.4'''-tetrasulfonate is obtained in a good yield.

HANS HOYER.
HANS COLOMBARA.
BERTHOLD BIENERT.