Pigments With Improved Properties

-Microreaction Technology as a New Approach for Synthesis of Pigments-

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Summary: Clariant, as an important pigment producer forces the investigation of new pigments with improved qualities and properties to fulfill the rising tomorrow's demands of customers. For these reasons, new production ways like microreaction technology are included. This paper focuses on results obtained in manufacturing pigments in a lab-scale microreactor as well as in a microreactor pilot plant. Investigations of the diazotation, azo-coupling and laking steps of pigments have shown not only the principle feasibility of these reactions in laboratory microreactors but also significant improvement of coloristic properties. The microreactor pilot plant, realized by the concept of numbering-up instead of conventional scaling-up process, allowed more detailed investigations of the complete azo-pigments synthesis under production conditions.

Keywords: Pigments, coloristics, microreactor, numbering-up, pilot plant

1. Introduction

In the last two decades powerful processes have been developed for fabrication of three–dimensional microdevices from a wide variety of materials. Recently, microdevices have become highly interesting for chemical, pharmaceutical and biotechnical applications [1]. Nowadays so-called microreactors with channel dimensions in the sub-micrometer range are a state of the art tool for R&D [2-5].

Due to the microchannels, microdevices are normally restricted to gas/gas, liquid/liquid and gas/liquid reactions. Investigations on reactions done in microreactors involving or forming solid substances are quite rare. For example scientists at Institut für Microtechnik Mainz (IMM)[1] reported generation of micro- and nanoscale solid particles in IMM's interdigital micromixer like precipitation of copper oxalate. Although there is a strong bias that solids or pigment suspension will block microchannels, Clariant decided to check out the basic feasibility of pigments syntheses by using microreactors.

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Microreactors, recognized by experts as a tool for process intensification by increasing mixing efficiency, have a high potential for application in the field of pigments technology. Producing pigments in microreactors may turn to profit to two respects. The main aspect is to fulfill customers demand on quality and properties for pigments of tomorrow. Intensified process conditions seem to allow yielding pigments with better application properties like coloristics (color strength, transparency, brightness and purity). Another aspect is to develop a continuous economic production technology for manufacturing of ordinary pigment volumes. The chemical industry's conventional approach of reducing production costs by economies of scale with larger plants could be challenged in future by another strategy. If industrial output via microreactors are demanded, several units have to be operated in parallel. This option makes possible to respond flexibly to changing demands by switching individual reactors on or off – in other words "production on demand" becomes feasible. Therefore, this work deals first with a principal feasibility study of producing azo-pigments in a laboratory microreactor. Additionally, the transfer of this technology to pilot plant scale to manufacture industrial quantities of azo-pigments with constant high quality is evaluated. For this, producing pigments in a pilot plant based on microreactors was investigated.

2. Evaluated microdevices

Figure 1 shows two CPC[2]-microreactor types used in this project. Upper right, you see a laboratory microreactor and at the bottom a microreactor that is mounted in a pilot plant. Letters (a) to (c) indicate in- and outlets for feed and products.

The microreactors are assembled of microstructured platelets mounted together by metallic bonding. Each platelet has numerous parallel channels in the sub-millimeter range with a special function such as

- dividing reactants into substreams and leading them into reaction channels,
- keeping reaction temperature within a desired range by cooling or heating,
- collecting product substreams and leading them out of the microreactor.

Based on a numbering-up concept [6] the microreactor pilot plant allows a higher output of several tons of pigment. This concept was realized by manifolding the reaction plane several times inside the microreactor and by operating several of those microreactors in parallel embedded in one housing. Additionally, the dimensions of the reaction channels have been slightly increased, but without changing the laminar flow conditions and especially without changing the mixing process. Adaptation of the channel geometries has also been done to maintain isothermal conditions for the reaction in respect to the increased product output.

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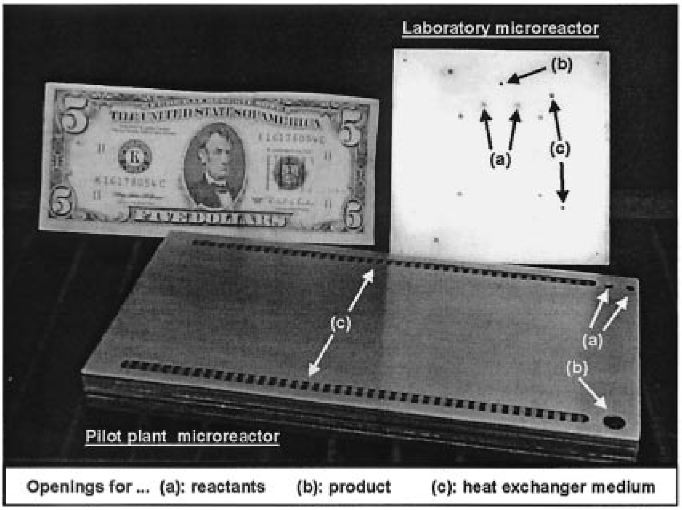


Figure 1. Laboratory and pilot plant microreactor

The laboratory and pilot plant microreactor have the same contacting principle of the reactants in common, shown in Figure 2.

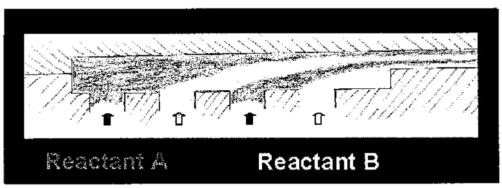


Figure 2. Sketch of microreactors contacting principle

Feeding the reactants onto each other leads to a multilamination. Mass transfer between these formed lamellas is due to molecular diffusion, which is an extremely fast process. To operate the microreactors, they are embedded in housings (see Figure 3) and equipped with pumps, heating bath and vessels (not shown as conventional laboratory equipment).

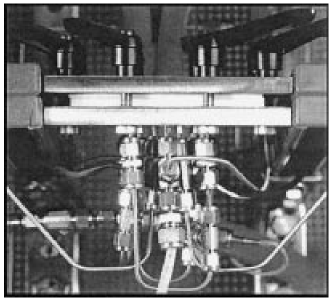


Figure 3. Housing and fittings of the laboratory microreactor

The Laboratory microreactor and the pilot plant allow investigating a continuous 3-step synthesis of azo-pigments – i.e. all three reaction steps like diazotation, coupling and laking are included – (see Figure 4). The key components of each reaction stage are microreactors embedded in one housing, several pumps and a corresponding number of vessels. The latter are for supplying educts and withdrawing product at the same time.

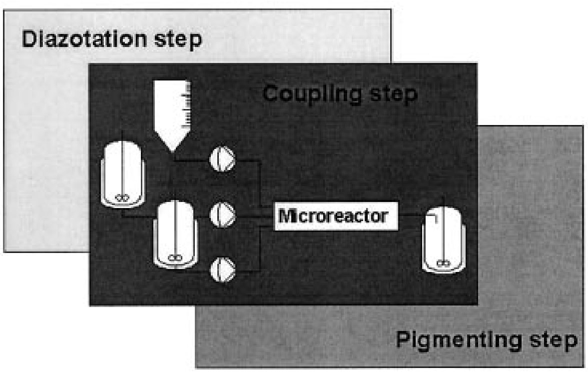
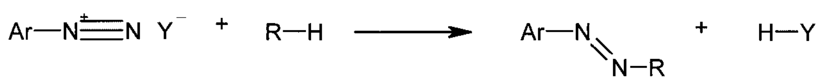


Figure 4. Flow sheet of the microreactor pilot plant experimental set-up

3. Pigments syntheses using lab-scale microreactor

To study syntheses of azo-pigments in microreactors with better properties two model pigments have been chosen, called model pigment 1 and 2, respectively. The first one is red coloured and the second one yellow coloured. Both pigments are synthesized by a 3-step reaction, i.e. diazotation, coupling and laking.

In the following the results of investigation of azo-coupling step of these two pigments are discussed. After reaction of a primary aromatic amine with sodium nitrite, the resulting diazo-solution / -suspension was fed together with a coupling agent into the microreactor at reaction temperature. The coupling reaction itself is an exothermic electrophilic substitution of a diazonium compound ($Ar-N\equiv NY$) with a coupling component (RH). The produced free acid (HY) is buffered by additional feeding a solution of sodium hydroxide into the microreactor or by using an internal buffer.



Ar : (Hetero) Aromatic group
R : Coupling component residue
Y : -Cl, $-HSO_4$

Model pigment 1: Diazo is a solution
Model pigment 2: Diazo is a suspension

Equation 1. Reaction scheme of the azo-coupling step [7]

Depending on the investigated pigment, flow rates of the raw materials were adjusted such that one of them could be analyzed in slight excess at the outlet of the microreactor. After coupling pigment suspension was worked up in a batch-wise comparable manner: separating the pigment from the yielded suspension, drying and milling. In the end, the pigment was tested and compared to the standard yielded in a batch process with respect to coloristic properties.

As there was no publication about producing pigments in microreactors, model pigment 1 was chosen for a first feasibility test. The reason for this procedure is, that in this case both reactants, i.e. diazo as well as coupling component, can be applied as solutions. This model pigment 1 is best to our knowledge the first pigment suspension produced inside a microreactor successfully. The product leaves the microreactor as deep red, highly viscous, almost pulpy suspension.

Table 1 shows comparison of the microreactor pigment with the standard of batch-wise produced pigment.

Table 1. Coloristic properties of microreactor model pigment 1 compared to the batch standard

	Microreactor Pigment 1
Color strength	119%
Brightness	5 steps glossier
Transparency	5 steps more transparent

As it can be taken out of table 1 microreactor model pigment 1 shows a tendency to more brightness as well as transparency compared to the standard. Higher transparency and an improved color strength of the microreactor pigment indicate smaller particle sizes, as will be shown later. The results indicated the possibilities for enhancements in product quality by using microreactors.

The next critical question to answer was, if one can also work with diazo-suspensions for coupling reactions in a microreactor. Therefore, model pigment 2 was chosen. Except the difference to feed now a diazo-suspension into the microreactor, the experimental procedures of producing model pigment 2 and 1, respectively, were the same. Also in this case, pigment suspension can be produced successfully: A diazo-suspension enters the microreactor and an intense yellow suspension leaves it. Furthermore, parameter studies show that coloristic properties of model pigment 2 yielded in the laboratory microreactor could be dramatically improved compared to the batch standard, i.e. conventionally produced pigment. Table 2 gives an idea about this.

Table 2. Coloristic properties of microreactor model pigment 2 compared to the batch standard

	Microreactor Pigment 2
Color strength	140%
Brightness	6 steps glossier
Transparency	6 steps more transparent

These laboratory microreactor experiments indicate process intensification e.g. optimum mixing of the raw materials when using microreactors for pigments production. Due to small dimensions of the reaction channels the pathway of one reactant into the lamella of the other reactant is pretty short.

Additionally, a high specific surface area of the multilaminated flow enables nearly isothermal process conditions without local overheating and, thus, suppressing secondary reactions such as decomposing of the diazo component. The latter explains the found high brightness of the microreactor pigment. Furthermore, like already indicated when investigating model pigment 1, a pigment with very high color strength as well as transparency was produced. These coloristic properties correspond to small particles and a narrow particle size distribution.

The comparison of the very first results of a totally new technology with the results of conventional technology after 100 years of optimization is very promising for the application of microreactors in the field of pigments synthesis. Furthermore, for conventional technology additional experimental work out is necessary when scaling-up the laboratory vessels to tank reactors. In contrast to this up-scale-struggle a huge advantage of microreaction technology is discussed in the scientific community for years: Numbering-up should avoid any risks in increasing production volumes. Unfortunately, experimental proof of this concept is rarely available. Therefore, the prerequisite for a successfull application of microdevices for industrial production of pigments is to prove that results of the laboratory microreactor are reproducible using a pilot plant based on microreactors.

4. Pigments syntheses using microreactor pilot plant

Azo-Pigments are traditionally produced in batch operations in large stirred vessels. After completing the reaction under defined reaction conditions, the resultant product suspension is further processed to produce the finished pigment. The advantages of batch processes in large stirred vessels – such as being able to change the production relatively rapidly – are however matched by some disadvantages in process control which often can have an effect on pigment quality. E.g. the formation of undesired by-products are due to reasons like hot-spots, non-uniform reactant concentration and backmixing.

In contrast to conventional scaling-up of batch process by enlargement of operation volume, microreaction technology achieves higher output by numbering-up of the operated microreactors [6]. Along this concept, there is no significant change of reaction channel geometry and, thus, of flow regime, although capacity was increased. Thanks to very small dimensions of the microchannels the stoichiometric ratio, temperature and residence time can be established very accurately and if necessary, adjusted till the optimal operation points are achieved. Therefore, no change of the achieved superior coloristic properties was expected when using identical parameters for pigments manufacturing in laboratory and pilot plant microreactors, respectively. This had to be proved and was finally shown for model pigment 2.

First, the pilot plant microreactor was designed and manufactured, in the second step a fully operable microreactor unit (including all peripheral equipment like pumps, vessels and piping to operate such a system in production environment) was built and in a third step the pigment synthesis was tested investigating model pigment 2. After bringing in operational use of the microreactor pilot plant process parameters and instrumentation (flowrates, sensor technology, reaction parameter control) in all three stages were optimized. Indeed, brightness and transparency of model pigment 2 produced in the microreactor pilot plant based on lab scale microreactors equal the values of the laboratory experiments (see table 2) and the color strength could even be further increased to 149%. This was primarily due to the used peripheral equipment. E.g. compared with the lab scale microreactor unit pumps were installed which are suitable for especially exact dosing of suspensions and for operating almost without pulsation. In this way, mixing efficiency as a the tool for process intensification could be enhanced at a very high level.

Figure 5 shows the coloristic results of model pigment 2 after running-up series and optimization of the continuous operation process. Now model pigment 2 can be produced with a constant quality at high level.

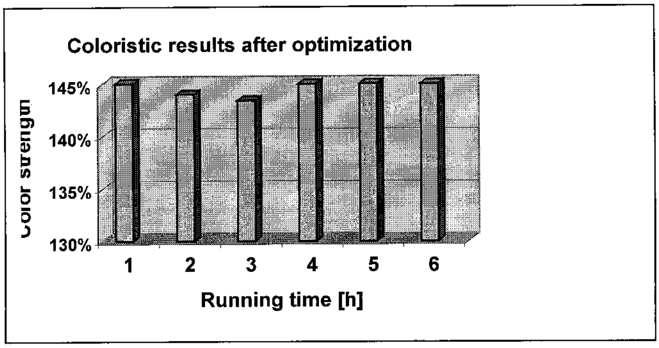


Figure 5. Coloristic results of model pigment 2 after optimization

Figure 6 shows a corresponding particle size distribution of the microreactor pilot plant pigment compared to the standard. Additionally, transmission electron microscope (TEM) pictures give a rough idea about a significant influence on pigment size of microreaction and batch pigments technology, respectively. Like indicated by coloristic properties, the particle size distribution of a microreactor pigment (1) is significant narrower than that one of the conventionally produced pigment (2) (standard deviation is s = 1.5 and s = 2, respectively). Also, the D_{50}-values differ by a factor of 6: Microreactor pigment has a D_{50}-value of 90 nm, the D_{50}-value of the standard batch pigment amounts nearly D_{50} = 600 nm.

In figure 7 the results of model pigment 2 yielded by numbering-up of microreactors are compared to data of the scaling-up phenomenon in batch operation. Increasing the reaction volume of batch syntheses color strength as well as color shade decreased at the same time. In contrast to this, there was no negative effect observed when realizing the numbering-up concept in the microreactor pilot plant. Therefore, nearly the same coloristic results were yielded under identical optimal operation parameters in the lab scale and pilot plant microreactor, respectively.

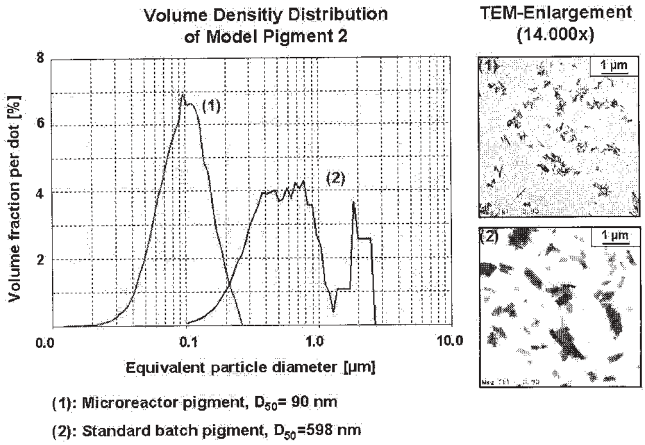


Figure 6. Comparison of model pigment 2 yielded in the pilot plant microreactor and batch standard pigment

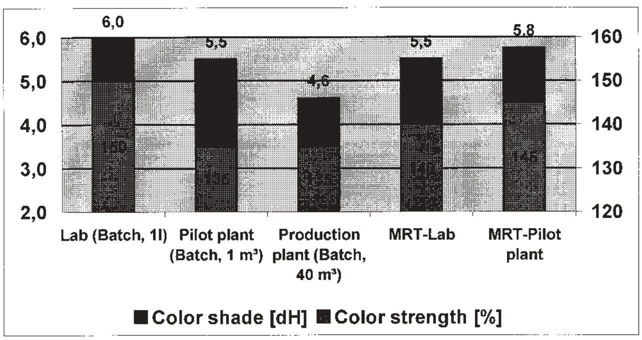


Figure 7. Coloristic results of model pigment 2 from scale-up operations compared with microreactor pigment

After reproducibility of laboratory experiments using the pilot plant is proved, there is at least one further hurdle to take. Regarding design and basic engineering of a pigment production plant, answers have to be found if fouling, coating or finally clogging of microdevices occur as well as how to minimize or to prevent these effects. Fouling of heat exchangers surfaces is still today an item of scientific investigations. Microdevices with its microstructures seem to be especially susceptible for fouling as well as coating. This would have a dramatic negative effect on

performance of the microdevice. The advantages of enhanced mass and heat transfer as well as continuously operating would be lost.
Therefore, during some 100 h nonstop runs of the pilot plant the performance of the microreactor under production conditions was analyzed. And indeed, with increasing running time of the pilot plant a steady rise of the pressure loss in the microchannels can be observed. But by a special technique, partial removal of coating out of the microreactor and a drop down of the pressure loss to the level at the beginning of starting the reaction is ensured. Although this process management is still under investigation a high process stability is obtained by using this technique.

5. Conclusion and outlook

The successful production of two typical, commercially relevant azo-pigments in lab-scale microreactors was demonstrated. Significantly improved coloristic properties were found. A pilot plant scale microreactor unit, realizing the concept of numbering-up instead of conventional scaling-up process, was assembled. The first experiment series show the reproducibility of the results found in the lab scale microdevice. Effects like fouling and clogging, in the past regarded as major problems for operating microreactors especially with respect to handling of suspensions can be managed from our experience. Future investigations will firstly focus on development of new pigments with special properties produced in microreactors and secondly on development of automated microreator units for production in industrial scale.

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