Stacking Behavior of Carbon Black on Cellulose Surface

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Abstract

Recently, pigmented inks became popular for personal and office printers. They have advantages in waterfastness and lightfastness, but they have limitations on rub resistance. Therefore, new inks have been required to overcome this problem.

Firstly, we investigate effects of additive in ink formulation. Secondly, pigments of hydrophobic surface are introduced. Finally, two pigments having different surface are applied for the optimum condition of additives for improving rub resistance, while maintaining optimum optical density.

As the result, we found that the hydrophobic pigments increased the rub resistance, moreover, preserving optimum optical density. The result of this study will be valuable for overcoming the weak point of pigment based inks.

1. INTRODUCTION

The ink requirements derive initially from the requirements of the imaging application being served by the ink system. The ink must be appropriate for the physical process used by the inkjet printhead, e.g., continuous inkjet with electrostatic drop deflection, drop-on-demand inkjet via piezoelectric or vapor-bubble pressure pulses. Successful ink for an inkjet process must also negotiate a large number of less obvious chemical and physical processes.

Ink jet printing systems have been developed as a target getting print quality of silver halide photographs. By developments of jetting smaller drop, coating media, and inks, ink jet printers became to be able to achieve high level print quality over silver halide photographs.

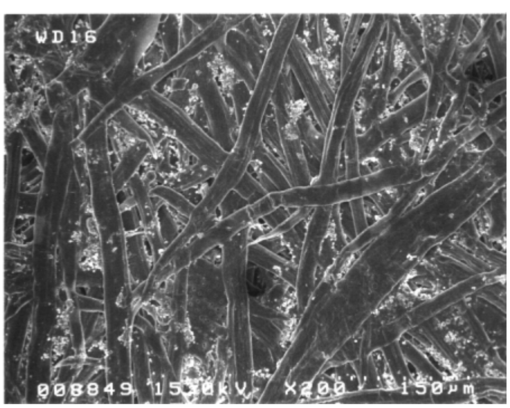


Fig. 1. Structure of cellulose on plain paper

The image medium, the substrate that carries the image, is a critical element of the inkjet technology. The interaction of the inkjet ink on plain paper is one of the most important characteristics for product success, as well as one of the most difficult to control. This is because plain paper is a very chaotic material in a physical sense and plain papers have widely different chemical properties. Fig.1 illustrates the tangled nest of fibers and voids that the ink encounters. Different paper mills, drawing from different fiber stocks, chemical, and process hardware, produce tangled nests with different void structures, fiber characteristics and surface chemistries.

Aqueous inkjet inks are designed to interact with these elements. They have viscosity and hydrophilic components that set up surface tension and capillary forces that pull the ink along the paper fibers and into the voids and fiber tubes. Image raggedness and show-through are just a reflection of the tangles and porosity of the paper structure. If the ink designer tries to stop the ink from entering the voids and fiber tubes, then drying times are unacceptable, and intercolor bleed becomes uncontrollable.

Aqueous inks are divided into groups by colorant type: dye, pigment, and heterophase colorant.

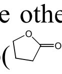
Water soluble dye based inks have strong points of bright and vivid color, wide color gamut and long time storage stability. But when using aqueous dye based inks, print qualities on plain paper are insufficient in waterfastness, lightfastness and sharpness.

To overcome these problems, aqueous pigmented inks have been developed. They have a clear advantage in lightfastness. The waterfastness of pigmented inks is also superior, provided the dispersion has not been made so stable that repeptization causing pigments to lift off the media occurs when the dried ink image is subjected to water. Since waterfastness performance is one of the primary reasons for choosing a pigmented ink.

One of the representative pigment is carbon black in inkjet ink area. The atomic structure of carbon black is similar to that of microcrystalline graphite which is composed of fused aromatic chains in series. In addition, the bulk structure of that is crystalline layer parcels and disorganized areas, which are interconnected with more particles. More than anything else, the surface of carbon black is important. In the manufacturing process, carbon black contains small quantities of chemisorbed oxygen on their surface. The oxygen exists in the form organic functional groups which include carboxyl acids and lactone group, among others.

Pigmented inks are more susceptible to smearing due to any forceful mechanical abrasions. Careful handling will not show any disruption of a dried image, but a forceful finger rub, especially if damp, will noticeably smear pigment into adjacent, nonimage, background areas.

To counteract this problem, pigment ink formulation incorporate a binder in some fashion. This can be an ink additive such as a latex, or a water-soluble polymer such as polyvinyl alcohol. But, the storage stability is sacrificed. The other solution is to increase the rate of penetration of ink into paper. But, the trade-off is that the lower optical density of the printed image is acquired.

So, we have selected two different type of pigment surface which is considered having different interaction strength with cellulose, in order to solve the above problems. The new pigment type has a more hydrophobic surface than commercially available one. Two types of pigments are shown below in Fig.2. One has hydrophilic surface composed of carboxylic acid group(-COOH), the other has hydrophobic surface composed of lactone group() and carboxylic acid.

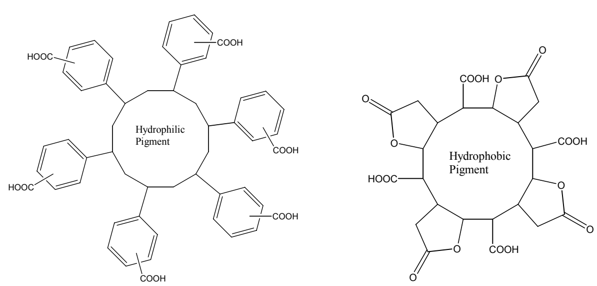


Fig. 2. Structure of pigments having two different surface

We have found the optimum condition of additives, using a response surface methodology which is a method of design of experiments. In addition, the hydrophobic pigment based inks increase the rub resistance, without sacrificing their optical density.

In this paper, we show effectiveness of additive ratio and new pigment type for enhancing rub resistance in our pigment based ink system, with maintaining optimum optical density.

2. EXPERIMENT

2.1. Materials

Table 1 shows a list of pigments which have different surface properties. The surface type is divided into hydrophilic or hydrophobic, according to groups attached to the surface of pigment.

Table 1. Pigment type classified by hydrophilicity

Full Name	Producer	Lactone: COOH (mol ratio)	Type
Cab-O-Jet 300	Cabot Co	0 : 1	hydrophilic
Bonjet Black CW-1	Orient Chemical Co.	0.68 : 1	hydrophobic
Bonjet Black CW-2		0.71: 1	
Bonjet Black CW-3		0.8 : 1	

Table 2 shows a list of additives which is classified by their functional group

Table 2. Type of additives classified by functional Group

Abbr. Name	Full Name	Purity	Producer	Type
IPA	Isopropyl Alcohol	99.5%	Kanto Chemical	Alcohol
DEG	Diethylene Glycol	99%	Aldrich	Diol
Gly	Glycerine	99%	Shinyo Pure Chemical	Triol
PEG	Polyethylen Glycol #600	99%	Kanto Chemical	Polyol
2-P	2-Pyrrolidone	99%	Aldrich	Amide
T-2-P	Tetrahydro-2-pyrimidone	97%	Aldrich	Amide
PC	Propylene Carbonate	99%	Aldrich	Lactone

2.2. Formulation

2.2.1. Preparation of Pigment Dispersion

To investigate effects of different pigment types, the components listed below(Table 3) were formulated, and the resulting dispersion was filtered through a 0.8um filter to remove dust and coarse particles. The only variable component is pigment and surfactant is needed for optimum surface tension.

Table 3. Pigment dispersion formulation

Pigment	Surfactant	water	Total
4	0.5	95.5	100

2.2.2. Preparation of Ink

Through screening test of additives in Table 2, we can derive three additives which are PEG, 2-P, and DEG as candidates, among others. To search for the optimum condition, response surface methodology (RSM) was introduced into design of experiments. Each additives which is PEG, 2-P, and DEG was included from 0 to 8 parts based on 100 parts by weight of the ink composition.

Table 4. Design of experiments by RSM

Pigment	Surfactant	PEG	2-P	DEG	water	Total
4	0.5	0~8	0~8	0~8	67~77	100

2.3. Print Quality Evaluation

Printing was carried out using the pigment dispersion and the test ink on a commercially available ink jet printer, MJC-3400P manufactured by Samsung Electronic Ltd.

Optical density and rub resistance of prints were evaluated in accordance with the following methods.

2.3.1. Optical Density

Solid test pattern (100% duty) was printed on plain paper (Samsung Recopy Paper) with the ink and dried spontaneously for 3 hours in a room.

Optical density of the print was measured with a GretagMacbeth densitometer (D196, manufactured by GretagMacbeth) at 5 different areas in the pattern and took an average value.

2.3.2 Rub Resistance

Solid test pattern (100% duty) was printed on plain paper (Shinho Recopy Paper) with the ink and dried spontaneously for 3 hours in a room. The printed surface was reciprocally rubbed 5 times with the same kind of paper using a rubfastness Test Jig which has a load of 1.3kg.

Optical density of the initial pattern was measured with a GretagMacbeth densitometer and then the optical density of the transferred, stained paper which is rubbed with overlapping printed pattern was measured.

An average value is calculated the percentage ratio of the transferred OD to the original OD. The lower calculated value means the better rub resistance.

Rub Value(%)=_transferred OD/ original OD

2.4. Molecular Model

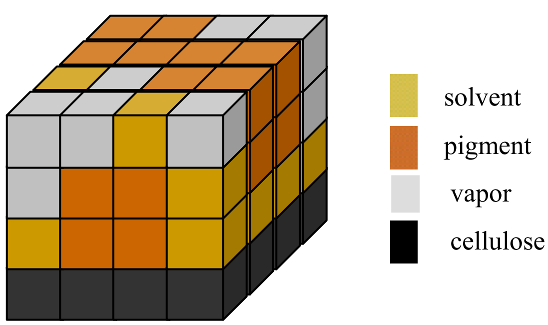


Fig. 3. Sketch of the cubic lattice of particle model

The solvent and pigment in our model are represented as a three-dimensional lattice on the surface of cellulose. A sketch of the lattice is shown in Fig.3. Each cell of a cube lattice can be occupied by solvent, pigment, vapor and cellulose. The lattice Hamiltonian can be expressed in terms of three binary variables, s_i, p_i, and c_i

Eq. 1.

$$H = \varepsilon_{ss}\sum_{<ij>} s_i s_j + \varepsilon_{sp}\sum_{<ij>} s_i p_j + \varepsilon_{pp}\sum_{<ij>} p_i p_j + \varepsilon_{sc}\sum_{<ij>} s_i c_j + \varepsilon_{pc}\sum_{<ij>} p_i c_j - \mu \sum_{i} s_i$$

where s_i, p_i, and c_i are roughly proportional to the density of the solvent, pigment, and cellulose at lattice site i, respectively. Each binary variable can equal to 0(low density) or 1(high density); however, a single lattice site cannot be occupied by more than one species.

The sum ($\sum_{<ij>}$) in Eq.1 includes only adjacent lattice cells. These cells attract one another with a strength that depends on the occupation of the two cells. The strength of the interactions between adjacent cells occupied by the solvent is determined by the energy density of the solvent and given by ε_{ss}. Similarly, when two adjacent cells are occupied by pigments they attract one another with a strength determined by the pigment interfacial energy given by ε_{pp}. Adjacent cells that are occupied by different species also attract one another. The strength of solvent-pigment, solvent-cellulose, and pigment-cellulose attractions are given by ε_{sp}, ε_{sc}, and ε_{pc}, respectively. Since the value of the solvent binary variables is fixed in the simulations reported below, we exclude the constant term $\varepsilon_{ss}\sum_{<ij>} s_i s_j$ from the Hamiltonian.

The last term on the right-hand side of Eq.1 includes the solvent chemical potential, μ, which is used to establish the average concentration of solvent and vapor cells at equilibrium. A large negative values of μ will favor evaporation.

Initially, the lattice is entirely filled with solvent and pigment particles, except for the first layer that is entirely filled with substrate cells, that is, cellulose. This lower layer is the only immobile layer, namely, the value of the cells in the lower layer is fixed for the entire simulation. Initially, pigment particles acquire random position inside the simulation box.

The pigment particles have negligible vapor pressure, and therefore, they execute a random walk on the three dimensional lattice, biased by their interactions with each other, with solvent cells, and with the substrate. Specifically, we attempt to displace a pigment particle by a single lattice spacing in a randomly chosen direction. Such a move is accepted, only if the region into which the pigment moves is completely filled with solvent. Solvent density in lattice cells overtaken by this displacement is regenerated in the wake of the moving pigment.

3. RESULT AND DISCUSSION

From this research, we have approached several important points, which will be explained the following each article in more detail. To put it briefly, the first stage is effects of additives in ink formulation, the second stage is effects of hydrophobicity on pigment surface, finally, the third stage is performance at optimization condition according to different surface structure of pigment.

3.1. Effects of Additives in Ink Formulation

In ink formulation, additives should be included because pigment dispersion doesn't give good printed images, besides, fast drying on a nozzle surface causes severe problem.

We can't apply all kinds of materials as an additive. So, we selected 7 common additives which are widely used for ink formulation, among others. Through screening test, we decided three candidate materials that have the high rub change per unit additive amount and that satisfy storage stability in relation to nozzle clogging.

Among three candidates, the one which has extremely high change for the rub value is utilized for showing its SEM photograph.

Then, three candidates are used for finding optimum ratio in ink formulation, through response surface methodology (RSM) as a design of experiments.

3.1.1 Selection of Candidates among common additives

We investigated effects for rub change when a unit amount of additive is applied, among alcohol (IPA), polyhyroxy compounds(DEG, Gly, PEG), cyclic amid compounds(2-P, T-2-P) and lactone(PC) as additives. The same pigment, C-300, was used for the ink composition. Table 5 shows the results.

Table 5. Additional effects of additives in Ink formulation

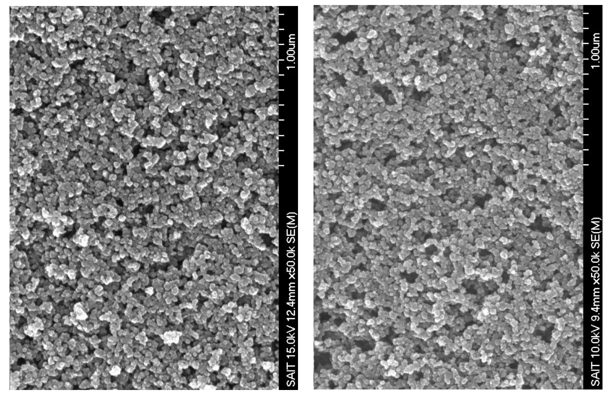
	$\lvert\Delta$ Rub.$\rvert$	Stability	Selection
IPA	4.5	X	
DEG	3.3	○	□
Gly	2.3	○	
PEG	13.3	○	□
2-P	7.9	○	□
T-2-P	9.9	X	
PC	3.4	□	

Among the additives, DEG, PEG and 2-P was chosen as additives for a optimization test. PEG has extremely high rub change per unit usage. Though T-2-P shows high rub change, its storage stability in relation to nozzle clogging is not satisfied, so, 2-P was selected. While DEG has relatively low rub change, it contributes storage stability, so accepted in our ink formulation.

3.1.2. SEM Photograph of Ink in Plain Paper

The SEM photographs of the surface of plain paper are shown in Fig.4. The images are printed when maximum & minimum amount of PEG are used for our ink formulation. C-300 is applied for that ink formulation, simultaneously.

We derive that the more PEG is used in our ink formulation, the coarser image is acquired. The more interactions between PEG and pigment molecules supposedly decelerate the penetration of ink into a plain paper, so the coarser structure is made up.



(A) (B)

Fig. 4. SEM photograph as a function of PEG:
(A) PEG, 8part (left), (B) PEG, 0part (right)
C-300 is used in (A) and (B).

3.1.3 Optimization of Additives by Response Surface Methodology

To search for the optimum condition, response surface methodology(RSM) was introduced into design of experiments. Each additive which is DEG, PEG and 2-P was included from 0 to 8 parts based on 100 parts by weight of the ink composition. Twenty inks are produced and evaluated by using the same pigment, C-300. Among them, the maximum & minimum values are represented below Table 6. We got the Rub. value from 35.7% to 62.6% and the OD from 1.53 to 1.62.

Table 6. Results of experiments by RSM

	Rub. (%)	OD
Max.	62.6	1.62
Min.	35.7	1.53

In case of C-300 pigment, the relations between the amount of each additive and the performance are shown in Fig.5.

The relations between the amount of each additive and the performance have been derived from experimental results. From those, we can expect overall tendencies, and predict a component ratio in ink formulation for getting a target performance. The red line is optimum condition for a target performance.

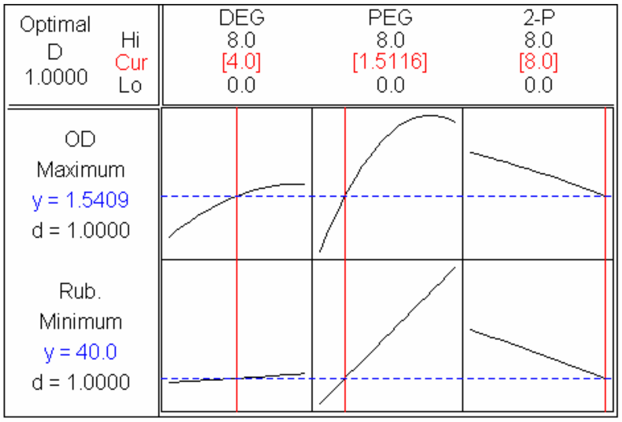


Fig. 5. Performance as a function of additive amounts in case of C-300 pigment. Red line shows a optimum condition for a target performance

3.2. Effects of Hydrophobicity on Pigment Surface

We are interested in pigment surface, especially, hydrophobicity. The hydrophobicity on pigment surface affects the stacking structure of that pigment. As a result, the coaser structure has lower rub resistance than the denser one.

New pigments which have different hydrophobicity were introduced. Physical properties of the hydrophobic pigment dispersion were examined and the performance of those were investigated.

A pair of SEM photographs will be shown to identify the pigment packing structure of printed image on the condition that there is big difference in rub value, but similar value in optical density. The reason of different packing structure is explained by 3D lattice Monte Carlo simulation model.

In each pigment, the optimum additive ratio in ink formulation is found through response surface methodology(RSM) as a design of experiments. Then, the performance results are represented at the optimum condition in comparison with those of prior optimization.

3.2.1. Physical Properties of Pigment Dispersion

The components listed Table 3 (Pigment Dispersion Formulation) were formulated. The only variable was pigment which was C-300, CW-1, CW-2 and CW-3, the other additives were same.

PB-1 ink which having hydrophilic pigment, C-300, has higher surface tension than PB-2, PB-3 and PB-4 ink in use of hydrophobic pigment, a series of CW Pigments. This results are supposed that more interaction with water molecules, when hydrophilic pigment is in use. So, it is difficult to separate the liquid surface and increase the surface tension of solution. Physical properties are shown in Table 7.

Table 7. Physical property & performance

Formula Name	PB-1	PB-2	PB-3	PB-4
Pigment Name	C-300	CW-2	CW-3	CW-1
Surface Tension (dyne/cm)	41.5	34.8	35.7	34.6
Optical Density	1.22	1.22	1.25	1.14
Rub Value (%)	49.44	38.79	23.62	21.62

We can also see the performance of pigment dispersion, according to different pigment, listed in Table 9.

Rub value is lower in using hydrophobic pigment than hydrophilic one. The more hydrophobic, the lower rub value is acquired, that is to say, the rub resistance is increased.

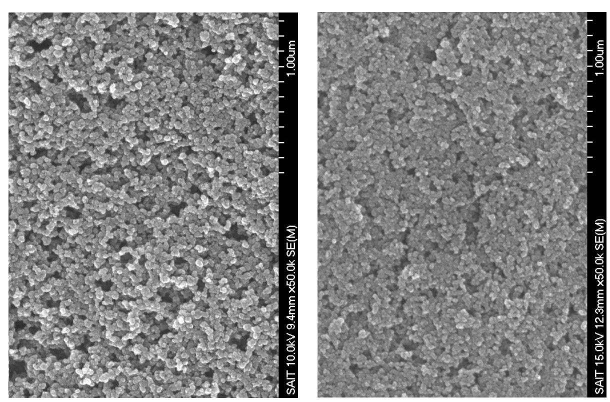
The optical density of pigment dispersions are relatively low, what is worse, the printed images are not satisfied because of bad coverage including white lines. Among them, though PB-4 has a lowest OD, but PB-1, PB-2 and PB-3 have the similar value.

So, PB-1 will be further compared with PB-3, because PB-3 has similar OD, but better rub resistance among PB2, PB-3, and PB-4.

3.2.2. SEM Photograph of Pigment Dispersion in Plain Paper

The SEM photographs of the surface of plain paper printed with PB-1 and PB-3 are shown in Fig.6. The PB-1 containing hydrophilic pigment, C-300, shows a coarse image, while PB-2 having hydrophobic pigment, CW-3, represents a dense one.

The more interactions with water molecules supposedly delay the penetration of pigment dispersion into a plain paper, when hydrophilic pigment is in use.



(A) (B)

Fig. 6. SEM photograph of PB-1(left), PB-3(right):
(A) C-300 ; hydrophilic pigment
(B) CW-3 ; hydrophobic pigment

3.2.3. Simulation Analysis

To apply for the 3D molecular model, we calculate each energy density ε_{pp} , ε_{sp} , ε_{sc} , and ε_{pc} , respectively.

Besides, we include only adjacent lattice cells to calculate. The sum ($\sum_{<ij>}$) in Eq.1. From those, the lattice Hamiltonian is computed as a function of the solvent chemical potential, μ. A large negative values of μ will favor evaporation.

In a typical ink drying experiment, drying mechanism occurs when the solvent evaporate or penetrate. Between the two, the drying process is mainly understood by solvent penetration mechanism to media. A large negative values of μ means that solvent penetrate so fast, that is, quick drying occurs.

In Fig.7, we can see simulation results for pigment stacking when inks are printed on plain paper, cellulose. For each pigment of which surface has different hydrophobicity, the lattice Hamiltonian is computed. Then, the final stacking structure is represented. A and B are front images C and D are cross sectional diagram. As shown SEM photograph in Fig.7, the hydrophobic pigment, CW-3, make a denser stacking structure than the hydrophilic pigment, C-300.

We determined two results of experiment and simulation coincided. We can assume the strong relation between hydrophobicity of pigment and stack structure on cellulose by simulation.

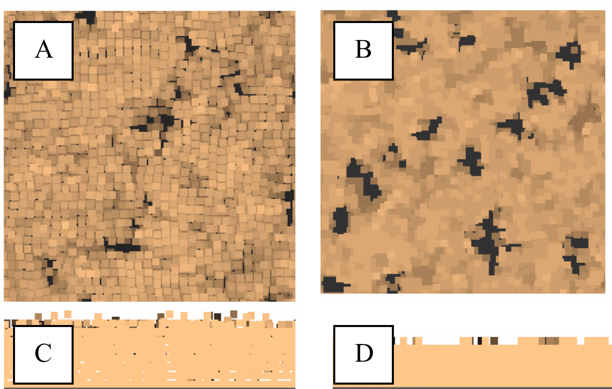


Fig. 7. Result of simulation using different pigment type on cellulose
A : C-300, B : CW-3 (front view of pigment stacking)
C : C-300, D : CW-3 (cross section of pigment stacking)

3.3 Performance at Optimization Condition according to a different Pigment

In each pigment, the optimum additive ratio in ink formulation is found through response surface methodology(RSM) as a design of experiments. Before and after optimization, the performance results are shown in Table 8.

From those results, we can derive that the relatively hydrophobic pigment, CW-3, based ink represents lower rub value than the relatively hydrophilic pigment, C-300, based ink. Namely, the hydrophobic pigment is supposed to enhance the rub resistance in ink formulation with maintaining optimum optical density.

In addition to that, additive ratio in ink formulation can improve rub resistance, so, the process of finding optimum condition of additives is very important. For each pigment of which surface has different hydrophobicity, there exist different optimum condition that we should find out case by case.

Table 8. Performance at Optimization Condition

Pigment	Before Optimization		After Optimization	
	Rub.	OD	Rub.	OD
C-300	64.6	1.63	41.7	1.56
CW-3	37.9	1.61	23.2	1.52

4 CONCLUSION

The hydrophobic pigment which has more hydrophobic groups around its surface has been developed in inkjet ink system for improving rub resistance on plain paper. In addition to that, using a response surface methodology as a design of experiment, we found the optimum condition of additives for increasing rub resistance, with maintaining optical density.

In the near future, pigment based inks will be used widely on account of their durability, e.g. lightfastness & waterfastness. The result of this study will be valuable for overcoming the weak point of pigment based inks.

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Biographies

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