Development of Filterability Test Method for Gel Retention Performance for UV Curable Ink Jet Inks

Masato Sumiya, Katsuhisa Yamada; Nihon Pall Ltd., Ami-machi, Ibaraki, Japan

Abstract

The purpose of this study was to provide a test method for gel retention performance of nonwoven filters for UV curable ink jet inks. Gel marked with elemental silver was formed from simulated UV curable ink. The silver marked gel was dispersed in the simulated UV curable ink by ultrasonic vibration. Large size gels were removed by pre-filtration with a track-etched membrane filter which had uniform 10 µm round shaped pores. Then the ink was subjected to filterability test to determine gel retention. Mass of silver element accumulated on filter medium was measured by ICP-MS after filter medium was dissolved in hot acid.

Gel retention performance of nonwoven filters was compared as demonstration of effectiveness of this method. Characteristics of the gel in dynamic viscoelasticity, size and silver element release were investigated as well.

Introduction

UV curable ink jet inks, which include photopolymerization initiators, sometimes accidentally form gel contaminants by polymerization with radicals induced from the initiators exposed to stray light energy and/or heat energy [1, 2] . Those gels have been considered one of the causes of nozzle clogging and coating defects; both critical image quality issues [3]. Filtration has been playing a key role to remove gels from the UV curable ink jet inks in printing processes and is expected to be improved and optimized further. Evaluation of gel retention performance is important for improvement and optimization of filtration. However, no proper method to handle gels and no quantitative gel retention study has been reported by the imaging industries.

The purpose of this study is to provide a new test method for gel retention performance for UV curable ink jet inks. Development of the test consisted of three steps (a) formation of gel, (b) marking gel with silver marker followed by dispersion and size control of gel, (c) filtration and measurement of silver element.

(a) Fluorescent light was adapted to irradiate weak UV radiation on simulated UV curable ink for gel formation. Exposure methods of the simulated UV curable ink were examined and a method was considered to provide gel available for the test. Dynamic viscoelasticity of the gel was measured to show its characteristics.

(b) Next elemental silver dissolved in base oil was mixed with the simulated UV curable ink to obtain silver marked gel. Influence of base oil mixing on gel formation was investigated. The silver marked gel was dispersed in the simulated UV curable ink. Then gel size was adjusted by pre-filtration. In the manufacturing process, the typical size of gel is estimated to be smaller than 10 µm. Those gels causing failure in printing mode should be removed by filtration.

(c) Finally the ink was subjected to filterability test. Mass of silver element accumulated on filter medium was measured by inductively coupled plasma-mass spectrometry (ICP-MS) after filter medium was dissolved in hot acid. Measurement of elemental metal was considered a good quantitative indicator for gel retention of a filter [4, 5] where the gel has been marked with elemental metal. Marking by noble metals such as silver had an advantage of low possibility of environmental contamination. By using this method, range of gel size and silver element release from gels were estimated. As demonstration of effectiveness of this method, gel retention performance of nonwoven filters was confirmed.

Materials and methods

Test flow

Flow of each test step is shown in Figure 1. Details of the procedures will be described in the following sections.

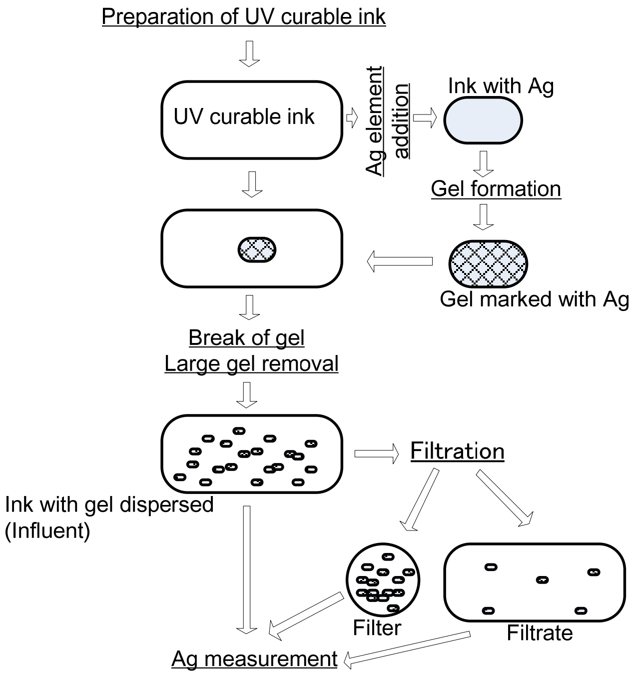

Figure 1.*Schematic of test flow*

Fluid preparation

A simulated UV curable ink was prepared, which had similar formulation to typical UV curable ink jet ink except for the absence of pigment. The formulation is shown in Table 1. The reagents were mixed at 65 °C and cooled down to ambient temperature under continuous stirring by propeller mixer for 15 hours. The procedures were operated in a dark room. Low toxicity monomers were selected for handling at filterability test. The ink was filtered by 0.45 µm porous nylon 6,6 membrane filter to remove contaminants of rigid particles and gels. The viscosity and the surface tension were measured by vibration viscometer SV-10 (A&D) and surface tension meter DF-300 (Kyowa Kaimenkagaku).

Table 1: Formulation of simulated UV curable ink

Function	Reagent	Mass-%
Pigment	-	0
Monomer	N-vinyl-ἐ-caprolactam Monomer A Monomer B	25.0 30.0 31.3
Stabilizer	Dimethylaminoethyl acrylate	0.1
Thermo-polymerization inhibitor	BHT	0.05
Photo-polymerization initiator	Lucirin TPO Phenylbenzophenone Irgacure 184	8.5 3.0 2.0
Surfactant	Silicon oil KF-351A	0.05

Gel formation

Influence of temperature and room light

As preliminary test for investigating influence of temperature and light on gel formation, 100 g of the ink was filled into two glass bottles. One bottle was kept at 40 °C for 24 hours in a dark room and the other was kept under room light for 1.5 hours at ambient temperature. Then the inks were filtered by 0.2 µm porous nylon 6,6 membrane filter under constant filtration pressure 45 kPa as shown in Figure 2. Mass of filtrate was continuously monitored to observe flow rate decline which would indicate generation of gels.

Exposure to fluorescent light at close range

To seek methods to obtain a large amount of gel, exposure of simulated UV curable ink to UV radiation from fluorescent light at close range was examined. A fluorescent light of round shape, 18W and white color was adapted. In Test A, 100 g of the ink was filled into a glass bottle to be exposed to UV ray as shown in Figure 3 (right). Intensity of UV light at 405 nm in wavelength was measured at 100 mm distance from the light source. A UV meter, UIT-201 with UVD-405PD sensor (USHIO) was used for measurement. The bottle was exposed to UV radiation for 20 minutes with shaking every two minutes by hand. In Test B, 100 g of the ink was poured in a cup to be exposed directly to UV ray from fluorescent light under continuous stirring as shown in Figures 3 (left) and 4. The exposure time was limited to five minutes. Intensity of UV light at 405 nm was measured at the surface of the ink. After the exposure, both inks were filtered by 1 µm track- etched membrane filter under constant filtration pressure 45 kPa to observe flow rate decline. In Test C, the ink was exposed to UV radiation in the same way as in the Test B until all of the ink changed to gel. Liquid temperature was continuously monitored. Dynamic viscoelasticity of the gel was measured by viscoelasticity meter ARES (TA Instrument Japan).

Marking and dispersion of gel with silver marker

To mark gel by elemental silver, oil base standard Ag reagent 10000ppm (SCP Science), 1 g or 5 g was mixed in a total 100 g UV curable ink and fluorescent light was irradiated in the same way as in the previous gel formation Test C. A quantity of 3 g of silver-marked gel was mixed with 297 g of simulated UV curable ink and was broken into small pieces by ultrasonic vibration for 15 minutes followed by stirring for 30 minutes with magnetic stirrer. The ink/gel dispersion was filtered by 10µm tack-etched membrane filter to remove gels larger than 10µm and submitted to filtration test.

Filtration test

Estimation of gel size

To estimate total amount of gel and the size, UV curable ink with silver marked gel dispersed was filtered through 0.2 µm porous nylon 6,6 membrane filter until 100g of total throughput at constant pressure of 45 kPa was achieved. The mass of filtrate was continuously monitored by electronic balance. This filter was expected to retain most of the gel although it could not be applied for actual ink jet ink because of pigment retention by tight pore structure. After filtration, mass of silver element accumulated on the filter was measured by dissolving the entire filter sample in hot acid followed by ICP-MS analysis. Both influent and the filtrate were submitted to the measurement as well. Further, filtrate of 1 µm track-etched membrane filter was obtained under the same filtration pressure 45 kPa for measurement of silver element amount.

Estimation of gel retention

Three kinds of nonwoven filters A, B, C were submitted to filtration test. All the filters were 1 µm rated which meant 99.98 % retention for larger than 1 µm rigid particles of standard test powder. Filtration and measurement were performed as in the same way in the previous test on 0.2 µm porous nylon 6,6 membrane filter. The influents were submitted to measurement of silver element amount. Based on those data, silver element retention equivalent to gel retention was calculated and compared.

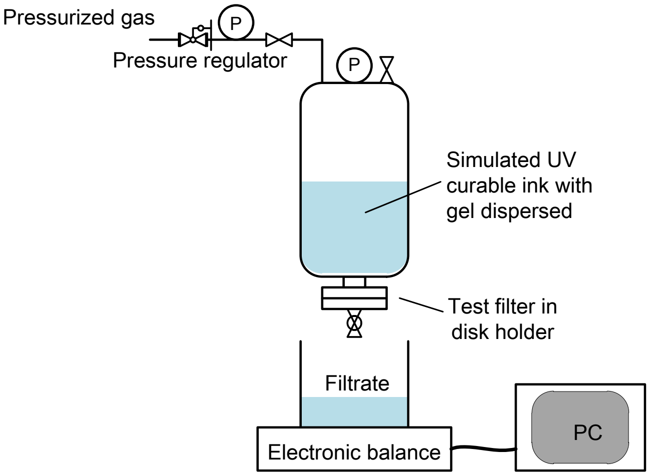

Figure 2*.Schematic of constant pressure filtration equipment. The mass of filtrate is measured by electronic balance to be stored at PC during filtration period. Size of test filter was 47 mm diameter.*

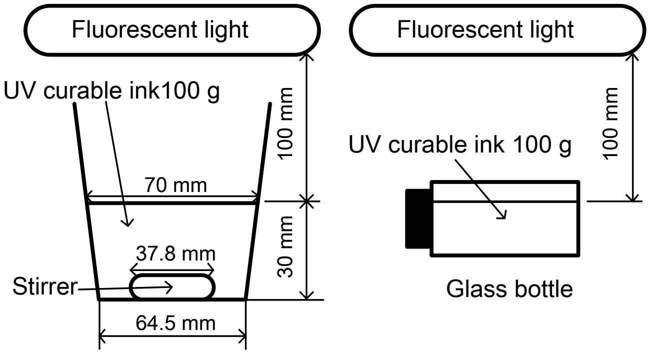

Figure 3*.Exposure through glass bottle to UV radiation from fluorescent light with shaken intermittently (right figure, Test A).Direct exposure to UV ray from fluorescent light with continuous stirring (left figure, Test B, C).*

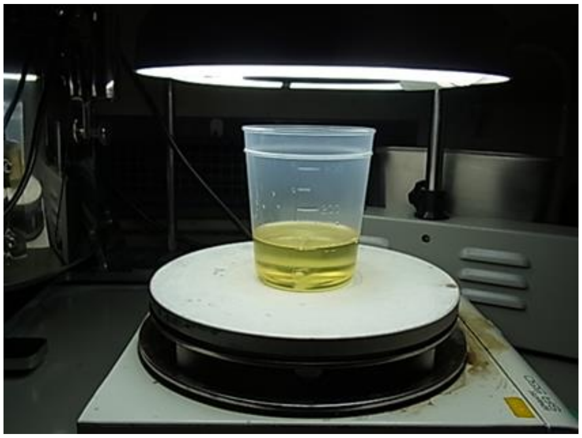

Figure 4*.Photo image of direct exposure to weak UV radiation from fluorescent light with continuous stirring.*

Results and Discussion

Fluid property

The viscosity of the simulated UV curable ink was 26 mPa•s at 22 °C and the surface tension was 34 mN/m at 20 °C. The viscosity and the surface tension were considered to be typical of UV curable ink jet inks.

Gel formation

Simulated UV curable inks were filtered by 0.2 μm porous nylon 6,6 membrane filter after they were kept at 40 °C for 24 hours in a dark room or exposed to weak UV radiation from room light for 1.5 hours to investigate influence of temperature and light on gel formation. The ink that had been kept under room light showed slight flow rate decline, an indicator of gel generation while the other ink kept at 40 °C did not show flow rate change. UV radiation from room light (fluorescent light) was considered to be effective for gel formation.

Simulated UV curable inks were exposed to UV radiation from fluorescent light at close range. Figure 5 shows results of filtration of the inks after exposure. The ink with exposure for 20 minutes through glass bottle (Test A) showed flow rate decline while the other ink with direct exposure for 5 minutes (Test B) showed no change. Direct exposure for longer than five minutes was tried for gel formation (Test C). Figure 6 shows increase of liquid temperature during direct exposure to UV radiation. Rapid temperature increase was observed at 12 minutes. Then all of the ink was found to have changed to gel. Chain reaction by radicals would have generated heat and caused temperature increase. A lump of UV gel obtained was stored in a glass bottle as shown in Figure 7. The gel appeared to be typical gel. Figure 8 shows dynamic viscoelasticity of the gel. Complex viscosity was extremely high at low angular frequency and went down as angular frequency increased. Storage modulus was higher than loss modulus and both moduli were stable. The viscoelasticity behavior observed was normal for gels [6].

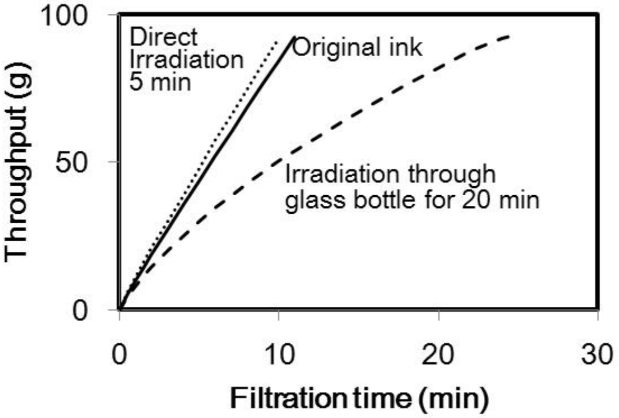

Figure 5*.Increase of throughput of 0.2 μm nylon 6, 6 porous membrane filter with filtration time in constant pressure filtration of simulated UV curable inks after exposure to weak UV radiation from fluorescent light (Test A, B). The Slope indicates flow rate. Filtration pressure was 45 kPa. Liquid temperature was 22 °C. Intensity of UV light at 405 nm during exposure was 0.23 mW/cm^2 at 100 mm distance from light source.*

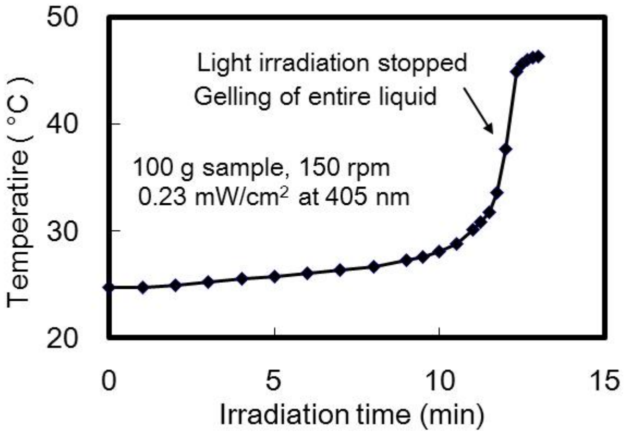

Figure 6.*Temperature change of simulated ink jet ink with irradiation time when the ink was exposed to UV radiation from fluorescent light at 100 mm distance (Test C).*

Figure 7.*Appearance of gel stored in glass bottle under UV radiation free light*

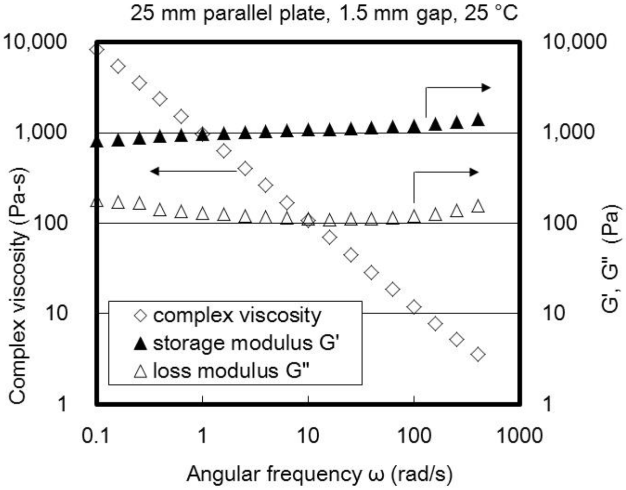

Figure 8.*Dynamic viscoelasticity of the gel. Change of complex viscosity, storage modulus and loss modulus with angular frequency.*

Marking gel with silver marker

Figure 9 shows temperature increase of simulated UV curable ink jet ink mixed with oil base standard Ag reagent during direct exposure to UV radiation in the same way as in the previous gel formation Test C. The ink with 5 g of Ag reagent did not show apparent temperature increase until 42 minutes. Then rapid temperature increase and conversion of all of the ink to gel were observed. Base oil mixed with UV curable ink would have inhibited chain reaction by radicals to a certain extent. The ink with 1 g of Ag reagent showed similar temperature increase and gel formation to the ink in Test C. Thus a lump of gel marked with elemental silver was obtained and the amount of standard Ag reagent was determined to be 1 g to 99 g of the ink.

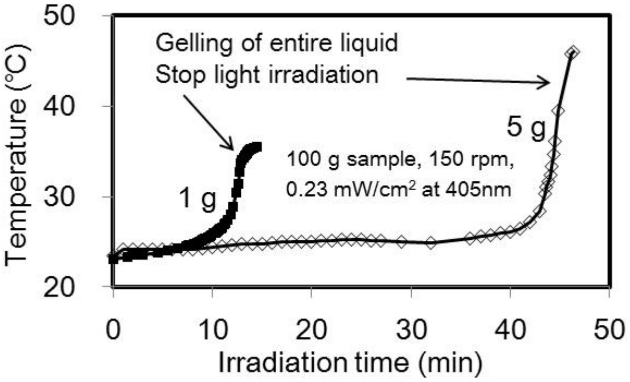

Figure 9.*Temperature change of simulated ink jet ink with irradiation time. The ink was exposed to UV radiation from fluorescent light at 100 mm distance after being mixed with oil base standard Ag reagent.*

Filtration test

Simulated UV curable ink with silver marked gel dispersed was prepared and submitted to filtration test as noted in the test method chapter. Figure 10 shows comparison of relative amount of silver element. Amount of silver in filtrate of 0.2 μm porous nylon 6,6 membrane filter was close to zero and the amount on the filter was close to that in influent. The results showed that almost all silver element was retained on the filter. The results also indicated that the silver element was not extracted to the ink and kept in gel structure because 0.2 μm porous nylon 6,6 membrane filter was not thought to adsorb free silver element dissolved in the ink. Based on the results, silver element retention rate was considered to be equivalent to gel retention rate. Figure 10 also shows that 70 % of silver element passed the 1 μm track-etched membrane filter. Most gels were thought to be smaller than 1 μm. Figure 11 shows SEM image of the 1 μm filter surface after filtration and exposure to intense UV ray for curing trapped gels and remained ink for SEM observation. Many small gels around 0.1 μm and aggregates of the small gels were observed. Filter pores were plugged with aggregates of gels.

Figure 12 shows typical flow rate change of test filter A, B and C during filtration of the simulated UV curable ink with silver marked gel dispersed. Flow rate of the filters tends to decline with total throughput. Filter C showed eminent flow decline, which would be the result of retaining a large amount of gel. Filter A and

B which had large porosity to hold gels showed relatively slow decline of flow rate. The mass of silver element on each filter and in the ink influents were measured. The calculated silver element retention rate is presented in Figure 13 as (equivalent to) gel retention rate. The same 1 µm rated filters showed different retention and generally higher retention than expected based on results for the 1 µm track-etched membrane.

As demonstrated in Figures 10 and 13, this test would be appropriate to distinguish gel retention performance of 1 µm or finer rated non-woven filters for UV curable inks with existence of large amount of smaller gels than 1 µm. This test would be available for seeking optimum conditions or optimum filter structure for gel retention as well.

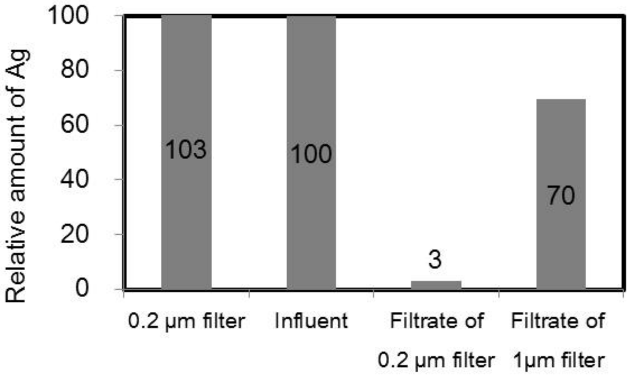

Figure 10. *Comparison of relative amount of silver element in the ink samples or on 0.2 µm porous nylon 6,6 membrane filter after filtering 100 g of the ink influent. The influent contained 33 µg silver elements in 100 g mass.*

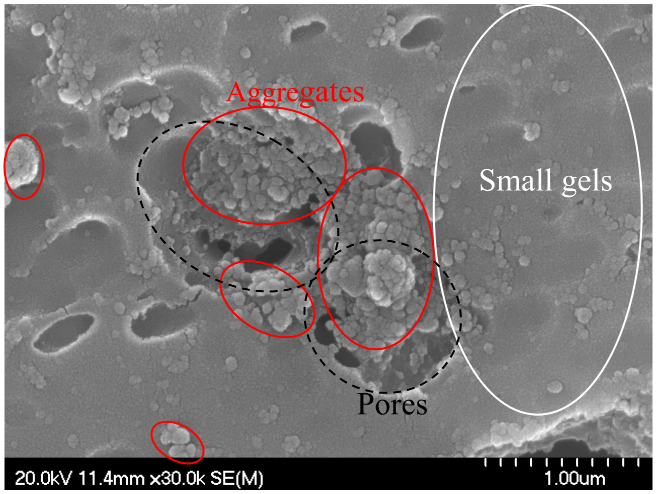

Figure 11. *SEM image of surface of 1 µm track-etched membrane filter after filtration of simulated UV curable ink with silver marked gel dispersed. The membrane was exposed to intense UV ray for curing the ink and gels for taking SEM image.*

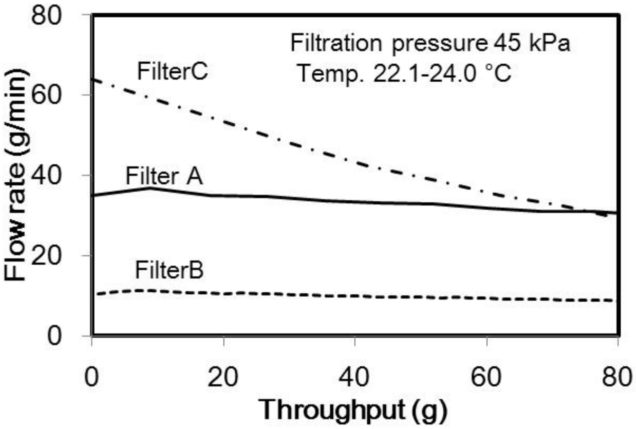

Figure 12. *Typical flow rate change of test filter A, B and C during filtration of the simulated UV curable ink with silver marked gel dispersed. Filtration was performed by constant pressure 45 kPa at liquid temperature 22.1 – 24.0 °C.*

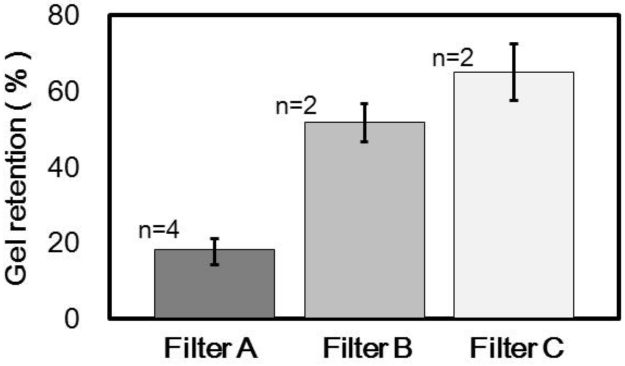

Figure 13. *Comparison of gel retention rate of filter A, B and C. Retention rate was calculated as (Ag on test filter / Ag in 100 g influent) x 100. Influents contained 30 – 40 µg of silver elements in 100 g mass. Error bar shows maximum and minimum value.*

Conclusions

Conditions for gel formation from UV curable ink have been investigated and silver marked gel was obtained. By using the gel, a test method for evaluating gel retention was developed by measuring mass of silver element accumulated on a filter as an indicator of gel capture. This method will be used for confirming gel retention performance of various non-woven filters which can be applied to UV inkjet ink. The authors believe this method will contribute to development of optimum filters and filtration to accelerate improvement of ink jet ink process.

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Author Biography

Masato Sumiya graduated from Hokkaido University and took his ME degree at graduate school of engineering, Hokkaido University in 1983. He joined Nihon Pall Ltd. in 1989 and has been working for evaluating filters applied to production of ink jet inks, electronic materials at SLS, global technical support division