Water repellent cotton surface through admicellar polymerization - a ZnO/fluoromonomer system

Sourav Mondal[1], Sukanta Pal[1], Jayanta Maity[1*]
[1]Research Scholar, [1] Research Scholar, [1*]Assistant Professor
[1]Department of Chemistry, Sidho-Kanho-Birsha University, Purulia 723104, West Bengal, India.

Abstract— This article reports the coating of fluorinated polymer with dispersion of zinc oxide nanoparticle to create both phase hydrophobicity using a simplistic way admicellar polymerization. Among the various methods used previously this polymerization technique provides tremendous result to impart hydrophobicty with short time. This polymeric coating showed the contact angle is 146^0. FT-IR analysis shows the presence of C-F bond. The surface morphology was examined by SEM, XRD analysis. XRD analysis demonstrates the presence of nanoparticle and SEM analysis revealed the distribution of nanoparticle on the cotton surface. TGA is used to show the temperature stability. Beside these wetting times, contact angle measurements confirmed the formation of thin layer of nanoparticle fluorine moieties on the cotton surface.

Index Terms— Admicellar Polymerization, Contact Angle, Fluoropolymer

I. INTRODUCTION

Nanoscience and nanotechnology combined have developed the material science and led to the evolution of a new range of improved materials including polymer and textile due to their nanoscale size preferentially have high surface area volume ratio and high surface energy. Nanotechnology has wide range of potential applications in microelectronics (Andres et al 1966); magnetic devices (Thomos 1988); photo catalysis (Kamat 2002) as well as medicine, plastics, aerospace and textile also. With the advent of nanoscience and nanotechnology, nanocoating on the surface of textiles, clothing has developed a new approach in textile industry for the production of highly active surfaces to have UV blocking, antibacterial [1], flame resistant [2] properties. Nanocrystalline ZnO is the most extensively used material for industrial as well as researchers due to their non toxicity, high temperature chemical stability and are photo-catalytic oxidation capability [3, 4]. A lot of nanocoating attempts such as plasma polymerization, pad dry cure, sonochemical process, sol-gel, layer by layer etc can develop multifunctionality, excellent durability and water resistance to fabrics. Nanoparticle dispersed in polymeric media i.e. polymeric nanocomposite has opened a new innovative coating finishes which benefits the development of multifunctional and intelligent high performance textiles. Xin et al. [5], Kiwi et al. [6], Zecchina et al. [7, 8] etc have respectively developedTiO_2 nanoparticle coatings on cotton fabrics to decompose contaminations such as dirt, stains, and harmful microorganisms. Bi Xu et al. [9] have prepared the superhydrophobic cotton fabrics based on SiO_2 nanoparticles and ZnOnanorod arrays with subsequent hydrophobic modification. Cotton a soft and floppy natural fibre is most extensively used material in textile industry. Water uptakes behaviour is the great disadvantages of cotton substrate and researchers have focused on this problem and tried to build up of water and dirt resistant fabrics i.e. self cleaning. Various treatment methods have been employed including spraying with fluoropolymer, siloxane plasma treatment with amines, layers by layers to impart hydrophobicity. Fluoro chemicals coating dominate the water repellence behaviour to fabrics by sufficiently lowering surface energy. Application of perfluorochemiclas can be performed in a variety of ways such as pulsed plasma polymerization of monomers with long perfluoroalkyl chains [10], chemical vapour deposition involving polymerization of perfluoromethylmethacrylate [11] to obtain a hydrophobic coating. In a very different approach direct fluorination of twaron fiber changed the nature of the fiber surface. [12] However all of them a versatile technique, admicellar polymerization is one of the best method to coat the cotton fabric by the formation of ultra thin film [13] of thickness on the order of 10 nm i.e. in nanoscale finishes without changing the softness, breathability characteristics of cotton fabrics. Admicellar polymerization has been successfully used to coat a polymeric thin film on different substrate such as polystyrene over alumina [14], polystyrene on cotton [13], polmethylmethacrylate on alumina pigment [15]. Admicellar polymerizations have superior advantages over the above process for its simplicity with low energy consumption when used on textile fabrics. It is a surfactant bilayer adsorption in situ polymerization reactions onto the substrate surface as well as a new method of hydrophobic as well as oleophobic finishing has been utilized as a guide for modifying the surface by forming on to it water insoluble continuous ultrathin polymeric film which is links to solid surface material by polar bonds. This film coating consists of four main steps, admicelle formation, monomer adsolubilization, polymeric film formation, and surfactant removal.

The objective of this paper is to study adsorption of fluorosurfactasnt and adsolubilization of fluoromethacrylates on a cotton surface by dispersing naomaterials to impart the water repellent function.

2. Experimental

2.1. Materials

Pique cotton fabric was purchased from local textile shop. The fabric was resized and treated in 10% NaOH solution for 1 hour and then the fabric was washed repeatedly until it was free from any remaining lubricants and other additives. The monomer used 2,2,3,3,4,4,5-octafluoropentylmethacrylate (OFPM) and 2,2,2-trifluoroethylmethacrylate (TFEM) were purchased from Sigma Aldrich. The surfactants used non-ionic Fluorosurfactant FS31 was purchased from DuPont India. The nanoparticle used is zinc oxide was purchased from Sigma Aldrich. The initiator potassium persulfate was purchased from Merck. All chemicals were used without further purification.

2.2. Coating process (admicellar polymerization)

Samples were prepared using admicellar polymerization process. Copolymerization of OFPM and TFEM on cotton was carried out in a 30ml vial containing 20-ml solution of 2500ppm FS31, OFPM,TFEM (4Mm), pH-4 water at temperature 40^{0}C. 1%NaCl is used for better surfactant adsorption. Zinc oxide nano particle is dispersed in water medium. At the start of the experiment, 1g cotton fabric was placed in the vial; vial was sealed with aluminum foil. The sealed vial was then placed in a thermo stated water bath at 40^{0}C and shaken at 80 rpm for 1 hour. Then an initiator Potassium persulfate was injected to initiate the polymerization to give an initiator: monomer ratio of 1:1. The vial

was resealed and the polymerization was allowed to proceed for an additional 1h at 60^0C. Excess surfactant was rinsed away with several volumes of water and the sample was dried in an oven at 70^0C. The sample formulations are given in Table 1.

Table1 Formulation of modified cotton as a function of surfactant amount for monomer: initiator (1:1)

Sample Name	Surfactant (ml)	Monomer (4Mm)		Initiator (4Mm) (ml)	Nano particle (1W %)	Water pH-4 (ml)
		OFPM (ml)	TFEM (ml)			
A	0.5	0	0	0	0	19.5
B	0.5	1	1	2	1	15.5
C	0.8	1	1	2	1	15.2
D	1.0	1	1	2	1	16.0
E	1.5	1	1	2	1	14.5
F	2.0	1	1	2	1	14.0
G	2.5	1	1	2	1	14.5

2.4 Characterization of treated cotton fabric

The aim of the current study was to study the chemical and physical surface changes of cotton fabrics using admicellar polymerization, and to identify appropriate conditions for evaluating the effects of polymerization on cotton fabrics. Scanning electron microscopy (SEM), wetting time analysis (water repellency test), contact angle analysis, FTIR-ATR spectroscopy, TGA, XRD are some of the tools that have enabled the observation of the nanoscale feature on the cotton surface. SEM is used to study the surface morphology of the coated cotton surface after admicellar polymerization. Fourier transform infrared attenuated total reflectance spectroscopy was used to analyze the chemical groups present in the polymer coating on the cotton surface. Thermogravimatric analysis was used to determine the temperature behaviour of the cotton substrate before and after modification. XRD represents the presence of zinc oxide nanoparticle in combined with SEM images modified and unmodified cotton fabric.

2.5 Water Repellency Tests

Two test methods were employed for assessing water repellency. An initial characterization of the treated surface was by the drop test. A 10 µL droplet of distilled water was placed on cotton fabric surface carefully with no force from a 20 µL syringe. Time for absorption of water (wetting time) on a fabric surface in the drop test was determined up to maximum of 30 min, at which point the sample passed. A second method was performed according to AATCC test method 22 (spray test).

2.6 Contact angle measurement

Contact angle measurement of the samples was tested by using an optical tensiometer (TL100 Theta) and software supplied with the instrument at 24^0C temperature. A 20 µL drop of distilled, deionized water of surface tension 72.75 mN/m was deposited on fabric by syringe from a height of 2 cm. Observations occurred over a 10min period with replicates at five different sites on the fabric and the average value was used. Results are given in Table 2.

2.7 Surface free energy measurement

Surface energy of the modified and unmodified cotton fabric was evaluated from the contact angle measurements to study the effects produced by the combined effect of nanoparticle/fluoropolymer composite coating. Different methods for surface energy analysis have been proposed in literature [16, 17].Here surface energy is determined from contact angle analysis by software (Attension Theta Lite 100) in our lab. Results are given in Table 3.

2.7 Surface characterization

For structural analysis, IR study of the different fabrics was performed using PerkinElmer (L1600300 Spectrum two Lita S.N.96499) FTIR- ATR spectrophotometer. The IR-spectrum was taken over the wave number range of 4,000 cm^{-1}–500 cm^{-1}. This study explains the functionalities present in different untreated and treated cotton fabrics. For surface morphology of the modified and unmodified cotton fabric was observed in a scanning electron microscope (SEM) Model No. Jeol JSM 5800 scanning microscope. The Thermogravimatric (TG) analysis was performed using PerkinElmer, S.N.5032010 instrument. TG studies were carried out as 5mg samples in alumina crucible. The pressure of nitrogen gas was adjusted at 2.0 bar. Temperature was increased from 50^0C to 500^0C at a heating rate 10^0C min^{-1}. X-ray diffraction of the pure cotton fabric and modified cotton fabric was carried out by X-ray diffraction analyzer Benchtop PROTO AXRD with CuKα target and Ni- filter in the range of 10 to 80. The diffraction patterns were scanned in steps of 0.02^0 at 2^0/min scan speed.

2. Result and discussion

Surfactants have a molecular structure composed of hydrophilic head group and hydrophobic tail group and can form stable nanoscale aggregates both in the solution and at interfaces. This aggregation is called admicells. When a typical organic monomer is embedded in to the solution, it will partition in to the core of the admicells in a process called adsolubilization in the presence of an initiator this monomer undergoes polymerization reaction to form a polymeric layer on the substrate of the surface (Fig.1). After the polymerization surfactant in the upper layer may be removed by washing to expose the polymeric layer on the substrate surface. A set of experiments carried out to obtain the hydrophobicity by using the fluorosurfactants and fluoropolymer and the obtained data could be discussed as follows. Hydrophobicity is very difficult to evaluate by only one method. The drop test enables a rapid and simple determination of water-repellent properties of fabric due to formation of the continuous, polymeric thin film on the cotton surface. To ascertain the water-repellency characteristics of the fabric, the resistance of the fabric to surface penetration by a spray and resistance to surface wetting should be measured. Tests have to be carried

out in combination with each other in order to obtain a complete understanding of performance. Samples were assessed for performance using drop test, spray test and contact angle measurement.

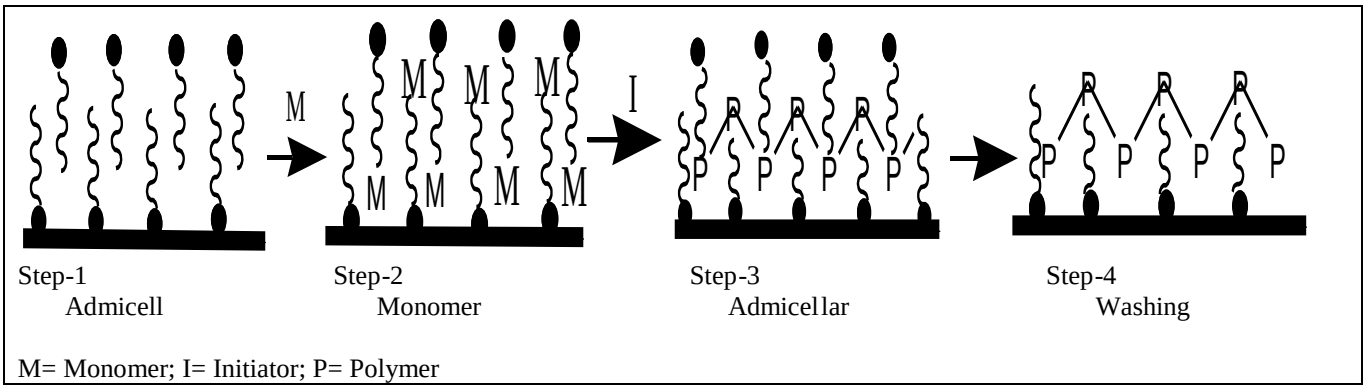

Figure 1 Scheme of admicellar polymerization

3.1 Drop test and contact angle measurement

Drops and rolls of water form spheres on cotton surface (Fig. 2) can highlights that hydrophobic film on the surface was created and it prevents water or moisture to penetrate through the surface. Contact angle measurements with water droplets revealed that modified sample effectively repelled water even after 60 to 90 minutes to allow reliable measurements attainable, apparent highest contact angle value was obtained 146^0 (Table 2). In table-2 it was seen that all cotton fabric sample shows contact angle greater than 90^0. This proves that all cotton surfaces are modified by coating and hydrophobic character generates. But the contact angle decreases when greater amount of surfactant used. A better result was obtained when we used 0.8 ml surfactant. This results deals with the surfactant adsorption and also the formation of polymeric thin film quality. This variation of surfactant provides a better result at a particular optimal surfactant level. Optimal surfactant level helps better surfactant adsorption on the solid/liquid interface by the formation of greater number of admicells and ultimately more polymer on the cotton surface resulting a better quality coating. As a result contact angle clearly indicates the formation of hydrophobic coating on the cotton fabric surface.

Table 2 Drop test results before and after admicellar polymerization

Sample Name	Contact angle	Stay time
A	0^0	0sec
B	132^0	>60 min
C	146^0	>90 min
D	144^0	>90 min
E	129^0	>60min
F	125^0	>60min
G	122^0	>60min

Figure 2 water droplets on cotton surface sample C

3.2 Infrared studies

In the FTIR spectra of modified cotton the minor changes are observed, indicating in admicellar process the internal bonds of in cotton fabric are not destroyed. FT-IR ATR spectra of untreated fabric and fluoromonomer treated fabric (Fig. 3) showed characteristic cellulose peaks around 1100-1200 cm^{-1}[18]. Other characteristic bands related to the chemical structure of cellulose were the hydrogen-bonded OH stretching at 3350-3200 cm^{-1}, the C-H stretching at 2900 cm^{-1}, and the C-H wagging at1314 cm^{-1} [18]. The OH bending of absorbed water was also observed in 1642cm^{-1}. Figure 3 show an absorbance at around 1751 cm^{-1} in the FT-IR ATR spectrum of fluorinated cotton, which might be the presence of the carbonyl stretching frequency of COF group. The frequency at 1010 cm^{-1} is a characteristic frequency of the C-F bond. Shih Hsien Yang et al. [19] has prepared a super-hydrophobic films using pulsed hexafluorobenzene plasma and showed a characteristic peaks around 999 cm^{-1} .The C-F stretching frequency is absent in case of untreated fabric but appears in the treated fabric indicating polar C-F bond between the cotton fabric and fluoromonomer. This data indicates that the hydrophobic cotton surface was achieved through copolymerization of the two monomers and fluorine is attached to the cotton surface which affects the water repellence

behaviour of the modified cotton fabric although the two monomers are different in chemical structure. This surface polymerization clearly implies that hydrophobicity is strictly related to the quantities of the attached copolymer to the cotton surface rather than their chemical composition.

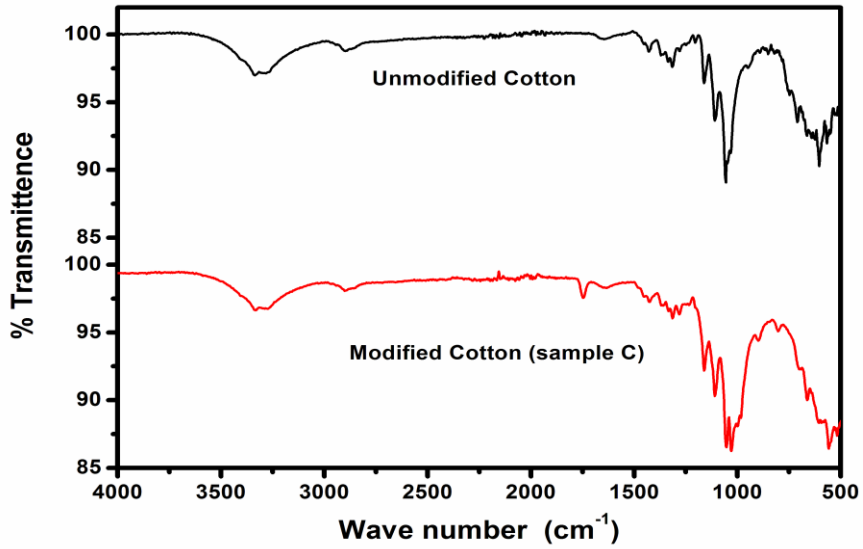

Figure 3 FTIR-ATR spectra: modified cotton fabric sample C, unmodified cotton fabric

3.3 Surface free energy analysis

Again from the surface energy calculation (Table 3) it is observed that surface fluorination by admicellar polymerization and deposited zinc oxide on cotton surface lowers the surface energy. Rougher surfaces later explained by SEM analysis exhibits higher contact angles with water, which is in turn related to low interfacial energy [20]. The surface energy of pure cotton substrate reported is relatively very high 46.2 Mm/m. The higher contact angle and lower surface energy suggests that fluorocarbon-fluorocarbon compounds are stronger than corresponding hydrocarbon compounds depending on the degree of interaction between the two compounds i.e. aggregation. As C-F bond is more electronegative and higher shielding efficiency of fluorine, the fluorosurfactant are more surface active and more hydrophobic comparing to hydrogenated surfactants by the aggregation of fluorosurfactant on the solid/water interface.

Table 3 Surface free energy analysis

Sample Name	Contact angle	Surface energy (mN/m)
B	132^0	5.760
C	146^0	1.893
D	144^0	2.079
E	129^0	7.351
F	125^0	8.873
G	122^0	10.337

3.4 TG analysis

Another also interesting property of the fluorine chemistry is that C-F bond energy is stronger than that of the corresponding C-H bond. This supports the TG experiment data. The plot of TG against temperature is shown in Fig. 4. From the plot it was observed that in case fluorinated cotton fabric weight loss starts at 330^0C but for nonfluorinated cotton fabric weight loss starts from 320^0C indicating that fluorinated cotton fabric is thermally more stable non-fluorinated fabric. That implies that fluorinated cotton fabric can behave as a flame retardant compound. Previously it is reported that growth of zinc oxide nano rods on cotton surface behaves an excellent flame retardant composite [21]. This work leads the increasing temperature is the combined caused of fluoropolymeric nano composite. The distribution of zinc oxide nano particle on the cotton surface can be explained from XRD analysis of the modified and unmodified cotton fabric.

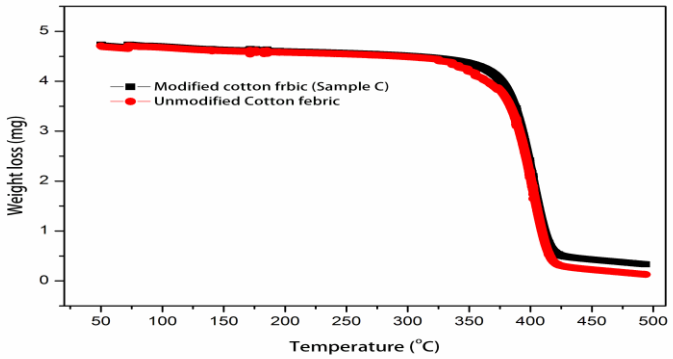

Figure 4 TGA graph modified cotton fabric sample C and unmodified cotton fabric

3.5 SEM analysis

In previous reports scanning electron microscopy (SEM) was used to observe the surface characteristics of cotton fibers. [22-24] The SEM images explain the difference between treated and non-treated samples at the fiber level. SEM imaging reveals the existence of a coating in addition to contact angle and wetting time analysis by providing pictorial evidence of the coating. Typical SEM images are shown in Figure: 5 before and after modification. It is previously reported that SEM images of the untreated cotton surface (Fig: 5a) has exposed characteristic parallel ridges and very smooth surface [24]. As shown in (Fig: 5b) the surface morphology of the treated cotton fabric was completely different from those of untreated one. The parallel ridges had almost vanished by admicellar polymerization and nanoparticle was embedded on the cotton surface to make the surface rougher. . These new character on cotton surface can be attributed to the formation of a thin fluorinated layer in the primary wall after treatment and some rearrangement occurs on the surface of cotton fabric after fluorination.

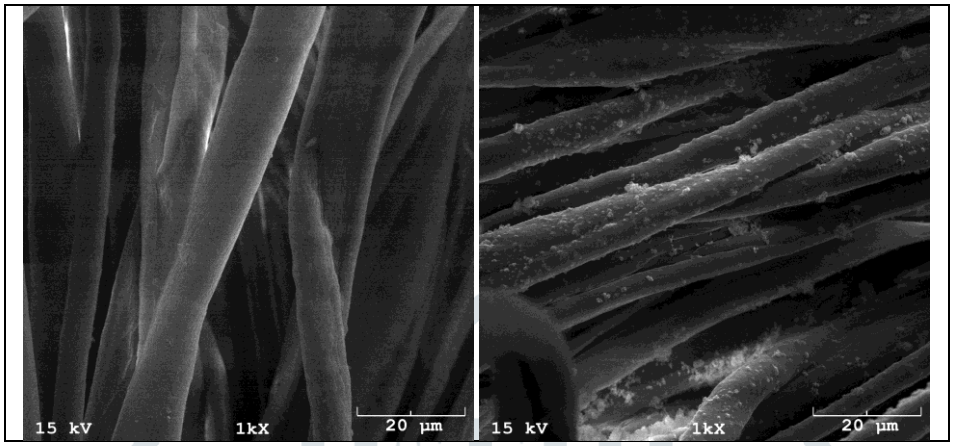

Figure 5 a) SEM image of unmodified cotton fabric and b) SEM image of ZnO-fluoropolymer modified cotton fabric sample C

3.6 XRD analysis

XRD is a useful supplement to SEM images to provide the information of probably physically adsorbed zinc oxide nanoparticle on the modified cotton surface. From XRD graph (Fig. 6b) it is likely to say that cotton surface was covered with ZnO nanoparticles with fluoropolymer coating. The diffractogram showed the typical peak $2\theta = 31.60^0, 34.50^0, 36.20^0, 47.53^0, 56.58^0, 62.78^0, 67.97^0$ due to the presence of ZnO nanoparticle on the cotton surface which are associated with (100), (002), (101), (102), (110), (103), (112) planes of the ZnO hexagonal wurtzite structure [25]. These results suggest the creation of thermoprotective layer on the cotton surface along with fluorination and improving the thermal stability.

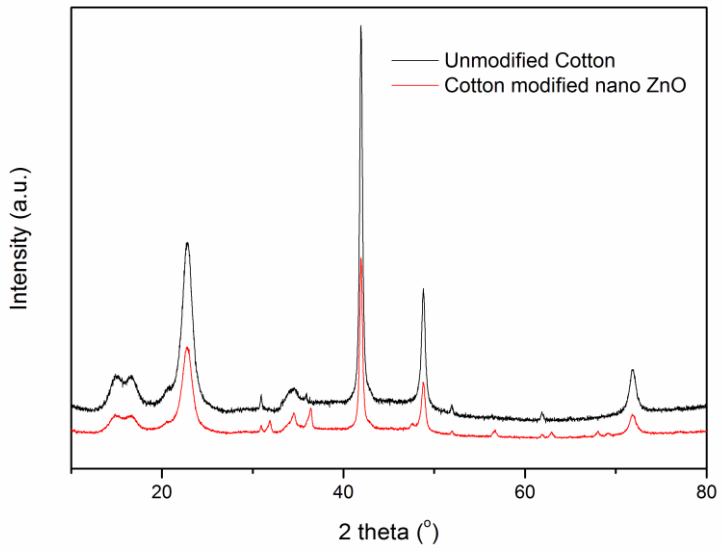

Figure 6 XRD of modified (sample C) and unmodified cotton fabric sample

3. Conclusion

In summary, we have successfully induced a hydrophobic treatment on the cotton fabric through the formation of an ultrathin fluoropolymeric layer along with water dispersible ZnO by admicellar polymerization. Wetting times of longer than 90 minutes and contact angles of 146^0 were observed. Optimal surfactant level, surface morphology and the structure of the modified cotton fabric revealed that rough surface is the key factor for hydrophobicity. This is a surfactant aided polymerization which creates great yields to surface roughness without changing the original cotton characteristics such as breathability and comfortability.

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