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Title; Application of a chemically adsorbed fluorocarbon film to improve demolding

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Application of a chemically adsorbed fluorocarbon film to Improve demolding

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Abstract

The use of an extremely thin chemically adsorbed fluorocarbon film (having a thickness of the order of 1 nm) for injection molding greatly reduces the ejection resistance, depending on the mold shape or dimensional accuracy.

Consequently, this technique should be very beneficial when applied to the

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molding of resin materials that have difficulty with mold release, such as silicone, urethane and elastomer resins. Further, this method will be useful for the molds used for making precision components that need to be highly accurate and ultra thin, such as optical components and chemical chips, for which conventional release agents cannot be used.

Keywords: Fluorocarbon film, Demolding, Injection molding, Chemical adsorption.

1. Introduction

Injection molding is already used for the mass production of optical components and medical devices. However, there is currently a need to improve injection molding and mold technology to enable them to produce highly accurate and detailed molds that can enhance the performance of the molded products [1-9]. Such a high level of detail and precision requires the use of fabrication techniques operating at the submicron level for the mold itself, in conjunction with highly effective demolding methods.

Although submicron-precision techniques for producing actual molds have now largely been achieved, an urgent need remains to improve demolding techniques [10, 11]. However, reports of the quantitative evaluation and measurement of the demolding resistance are rare [12-14]. For example, even if a mold is produced at submicron accuracy, current conventional release agents will permit a loss of mold shape, because the release agent coating gives rise to a loss in precision. If the release agent coating is

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made thinner, the lack of uniformity causes problems such as demolding difficulties.

In light of these circumstances, we attempted in this study to overcome the loss in mold precision and to facilitate demolding. To this end, we used a chemically adsorbed film process [13], which allows the even formation of a nanofilm, unaffected by the base shape, that would serve as the release film. The results of an evaluation of the actual injection molding performance using a test mold have already been described.

2. Experimental method

2.1 Apparatus

Figure 1 shows the dimensions of the molded product that was used to measure the ejection resistance in these experiments. Figure 2 shows a photograph of the molded product, while Figure3 provides a diagram of the die structure that we used for this experiment. The mold was constructed with two plate types, a single-cavity and a side-gate configuration, and had a half "S" shape to alleviate the effects of shrinkage of the runner on demolding.

The molded product was in the shape of a cap, with an internal diameter of 10 mm, an external diameter of 13 mm, a height of 9.5 mm, and a wall thickness of 1.5 mm. The internal sides were made straight so that demolding was difficult, and the external sides only were given a draft angle of 3°. An ejector pin with a diameter of 6 mm was attached to the center, and an indirect mold cavity pressure sensor (9221AA)

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(manufactured by Kistler Japan Co., Ltd.) was fitted under the ejector pin seating. The measurement data were recorded by software (Detaflow Light Ⅱ) and the ejection resistance in the ejector was evaluated.

The properties of the chemically adsorbed fluorocarbon films deposited on the mold were determined by measuring the static contact angles [16] with water drops that were about 1 μL in volume with a contact angle meter (Drop Master 700, Kyowa Interface Science Co., Ltd.). This meter permits the drop angles to be processed by computer. The three measurement points used depended on the die shape. The drop contact angles were measured within 5s so that the passage of time did not influence the data, and confirmed the water-repellent state of the film.

2.2 Preparation process of the chemically adsorbed fluorocarbon film

Fig.4 shows the process by which the chemically adsorbed fluorocarbon release films were formed on the surfaces of the test mold. The chemical agent used ($CF_3(CF_2)_7(CH_2)_2Si(OCH_3)_3$) was purchased from Kagawa Gakusei Venture Ltd.

First, the oil and dirt adhering to the die core pin were roughly washed with an ultrasonic die washing machine (CPE-30-P, Kuripipa-ace, Somax Co.,Ltd.), and then with another ultrasonic washing machine (USK-5R, AS-ONE Co., Ltd.) in pure water, chloroform and acetone for 5min for each solvent. Then, it was washed once more with ethanol and air-dried. Finally, after a corona discharge treatment was carried out (Multi-Dyne 1000, Navitas. C Co., Ltd.), the organic material on the surface was judged

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to have been completely removed. In addition, the wettability of the pin surface was improved.

After the above cleaning process, the chemically adsorbed film was formed by immersing the pin in the adsorption liquid for 1h. Any unreacted excess adsorbent remaining on the core pin surface was then removed by ultrasonic cleaning in chloroform for 5min, and then in acetone for 5min. Finally, the core pin was washed with ethanol, and following ultrasonic cleaning in pure water for 5min, dried by blowing dry air [17].

A schematic view of the chemically adsorbed fluorocarbon film formed on the surface of the pin is shown in Fig. 5. The adsorbent contains active trimethoxysilyl groups, the fluorocarbon functional group, and the space group consisting of a hydrocarbon chain. The active trimethoxy groups react with the active hydrogen of the hydroxyl groups (－OH) present on the die surface through the loss of methanol. In this way, a fluorocarbon film was formed directly on the substrate. In addition, as there are no active groups (such as hydroxyl groups) on the fluorocarbon film surface, no further additional chemically adsorbed films form.

2.3 Resin and molding conditions

A general purpose PMMA resin (Delpet 60N, Asahi Kasei Corporation) was selected for the following reasons.

The chemically adsorbed film is stable to a temperature of about 320°C (to 420°C

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in a nitrogen atmosphere). The PMMA resin is readily available, being commercially used for medical fluidic devices, optical disks, etc. and the condition of the molded piece (damage, cracks, etc.) after demolding can be easily evaluated.

The molding conditions used were as follows:

Mold temperature: 47°C (as measured).

Resin temperature: 240°C .

Peak pressure: 60 MPa.

2.4 Mold core pin and evaluation method

A photograph of mold core pin is shown in Fig. 6. The core pin was polished to a mirror finish; its surface roughness Ra and Rmax values were 0.05 μm and 0.68 μm, respectively. The ejection resistances of the core pins were measured with and without the chemically adsorbed film. The differences between them were compared and the demolding resistance and its rate of reduction were estimated.

2.5 Procedure

Step 1:

Initially, the operation of the ejector was checked without load (no molding), and the load was measured approximately 10 times with the force sensor. It was confirmed that no large (10N or greater) loads were needed.

Step 2:

After verifying the no-load operation, molding was conducted without the

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chemically adsorbed film in order to measure the initial core pin-specific ejection resistance. The product was molded approximately 200 times. As the molding was not stable for the first 10－20 times, the results in this interval were excluded from the experimental data.

Next, the chemically adsorbed film was prepared on the same core pin after cleaning, and a similar experiment was performed for 2000 moldings to confirm the effect of depositing the film. In addition, the durability of the chemically adsorbed film was evaluated using the same core pin, by continuing measurements and observations until a significant change occurred in the ejection resistance. The contact angles of water drops on the core pin were also measured at the point where there was a large change in the demolding resistance.

3. Experimental results and discussion

First, photographs of the water drops on the core pin before and after preparing the chemically adsorbed film are shown in Figs. 7 and 8, respectively. After initial cleaning, but before film deposition, the contact angle was approximately 80°. The contact angles of water drops were approximately 20° after the corona discharge treatment (Fig. 8(a)), indicating that the wettability was very much improved. On the other hand, the contact angle increased to approximately 115° after deposition of the film (Fig. 8(b)). This large change indicated that the film had in fact been formed.

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Furthermore, the contact angles were further improved to approximately 120° after the last washing (Fig. 8(c)), indicating that the monomolecular film had been completely formed.

Fig.9 shows the demolding resistance changes as a function of the number of molding shot with, and without, the film. The specific demolding resistance of the core pin without the chemically adsorbed film was about 340 N at between 0 and 230 shots. As the load resistance attributable to the ejector operation was from 4 to 7 N, their effect was negligible.

However, when the chemically adsorbed film was present, the demolding resistance was unstable and ranged from 200 to 250 N in the first 500 shots region. This unstable cause was considered because die temperature and a molding condition are not stabile. After about 500 shots, the demolding resistance stabilized at a level of about 150 N.

The effect of the film is very large, dropping the demolding resistance to about one-half of its value prior the film being deposited.

The results of the long-term durability test are shown in Fig.10. The specific demold resistance of the core pin without the chemically adsorbed film was first measured for 2000 shots using the same procedure as above as a reference. The initial demolding resistance was in the range of about 310－340N. After that test, the chemically adsorbed film was formed on the same core pin, and the demolding test

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continued. The results showed that the initial demolding resistance was 280N, and then the resistance dropped suddenly to 190N after 500 shots.

The similarity of this behavior to the short-term test indicates that the effect of die temperature and a molding condition were inconsistent in the region between 0 and 500 shots.

Afterwards, the demolding resistance gradually dropped to 170N between 500 and 2000 shots. In this region, the resistance was still somewhat unstable, but the positive effect of the chemically adsorbed film applied to the pin is clear. The resistance continued to range between 140 and 170N until 11,000 shots had accumulated, a value again roughly one-half of that prior to depositing the film.

Between about 11,000 and 11,500 shots the ejection resistance jumped up to about 250N, and then suddenly increased to about 280N after 13,000th shots. Fig.11 shows a photograph of a water drop on the core pin surface at this stage. The contact angle was approximately 85°. This low value indicates that the chemically adsorbed film had lost its effectiveness. The resin sludge and outgassing stuck to a core pin at this stage, and so the core pin was washed by the same method as washing after the chemically adsorbed film formed. As a result, the contact angle recovered to approximately 105°, as shown in Fig.12, showing that the chemically adsorbed film was still present.

To verify that the film was still effective after washing, the demolding test was restarted with the washed core pin. Referring to Fig.10, at this second stage, the

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initial demolding resistance was 280N, but it then steadily decreased until 13,100 shots.

The similarity of this behavior to the short-term test indicates that the effect of die temperature and a molding condition were inconsistent in same as the time of a start.

Afterward, The demolding resistance stabilized once more between 140N and 170N in the 13,100 - 20,000 shots region. At about 20,000 shots, the demolding resistance suddenly changed to about 250－340N, and never went back to 150N until the test was stopped after 25,000 shots.

Fig.13 shows the photograph of a water drop on the core pin surface at the conclusion of this third stage (25,000 shots). The contact angle of this water drop was approximately 90°. It was thought that the increase of the demolding resistance over 20,000 shots was caused by resin sludge or outgassing affecting the film, leading to the decision to stop the test at that stage. However, since the test was not continued with a rewashed pin, it is possible that the final rise in resistance is due to damage to the chemically adsorbed film.

Finally, Table 1 summarizes the relationship between the demolding resistance and the contact angle of water drops at several critical junctures during the tests. The demolding resistance increased with a decrease in the contact angle of water, indicating that the measurement of the static contact angles are useful for evaluating the effectiveness of the chemically adsorbed film in promoting demolding.

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4. Conclusions

(1) It was confirmed that a chemically adsorbed fluorocarbon film is very effective in improving the demolding performance by reducing the ejection resistance. In addition, the scratch and the crack, etc. could be prevented and this enabled it to improve the form accuracy of the mold, and surface coarseness.

(2) It was demonstrated that the chemically adsorbed film was durable in continuous use up to 10,000 shots, and also that the ejection resistance could be recovered at least once by washing.

(3) As the thickness of the chemically adsorbed film is around a few nanometers at most, and there is no irregularity in the film thickness, there is no loss of shape and accuracy in the dimensions of the mold [18].

Therefore, we conclude that a chemically adsorbed fluorocarbon film is extremely effective as a release agent for high-precision molds.

Acknowledgement

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Figure Captions

Table. 1. The relationship between the demolding resistance and the contact angle of water on a core pin at crucial times during the molding run.

Fig. 1. Dimensions of the molded product.

Fig. 2. Photograph of the molded product

Fig. 3. (a) Cross-section and (b) plan view of the mold die

Fig. 4. Process for the formation of the chemically adsorbed fluorocarbon films.

Fig. 5. Schematic view of a monolayer fluorocarbon film chemically absorbed on the pin substrate.

Fig. 6. The two types of mold core pin used in this study.

Fig. 7. Photograph of a water drop on a core pin after initial cleaning.

Fig. 8. Photograph of a water drop on a core pin: (a) after corona discharge processing (b) after coating with the fluorocarbon film and (c) after the final washing

Fig. 9. Short-term test of demolding resistance changes as a function of the number of molding shots.

Fig. 10. Long-term test of demolding resistance changes as a function of the number of molding shots.

Fig. 11. Photograph of a water droplet on the pin after 13,000 shots.

Fig. 12. Photograph of a water droplet on the pin after washing the die at 13,000 shots.

Fig. 13. Photograph of a water droplet on the pin at the end of the run (25,000 shots).

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Experimental state/Number of molding shots	Demolding resistance	Contact angle
Ejector operation load	4－7N	－
Untreated pin after initial washing	340N	80°
After corona discharge treatment	－	15°
Chemically adsorbed film treatment	－	115°
After final die washing	140－170N	120°
After 13,000 shots	280N	85°
After rewashing the die	140－170N	105°
After 20,000 shots	340N	90°

Table 1

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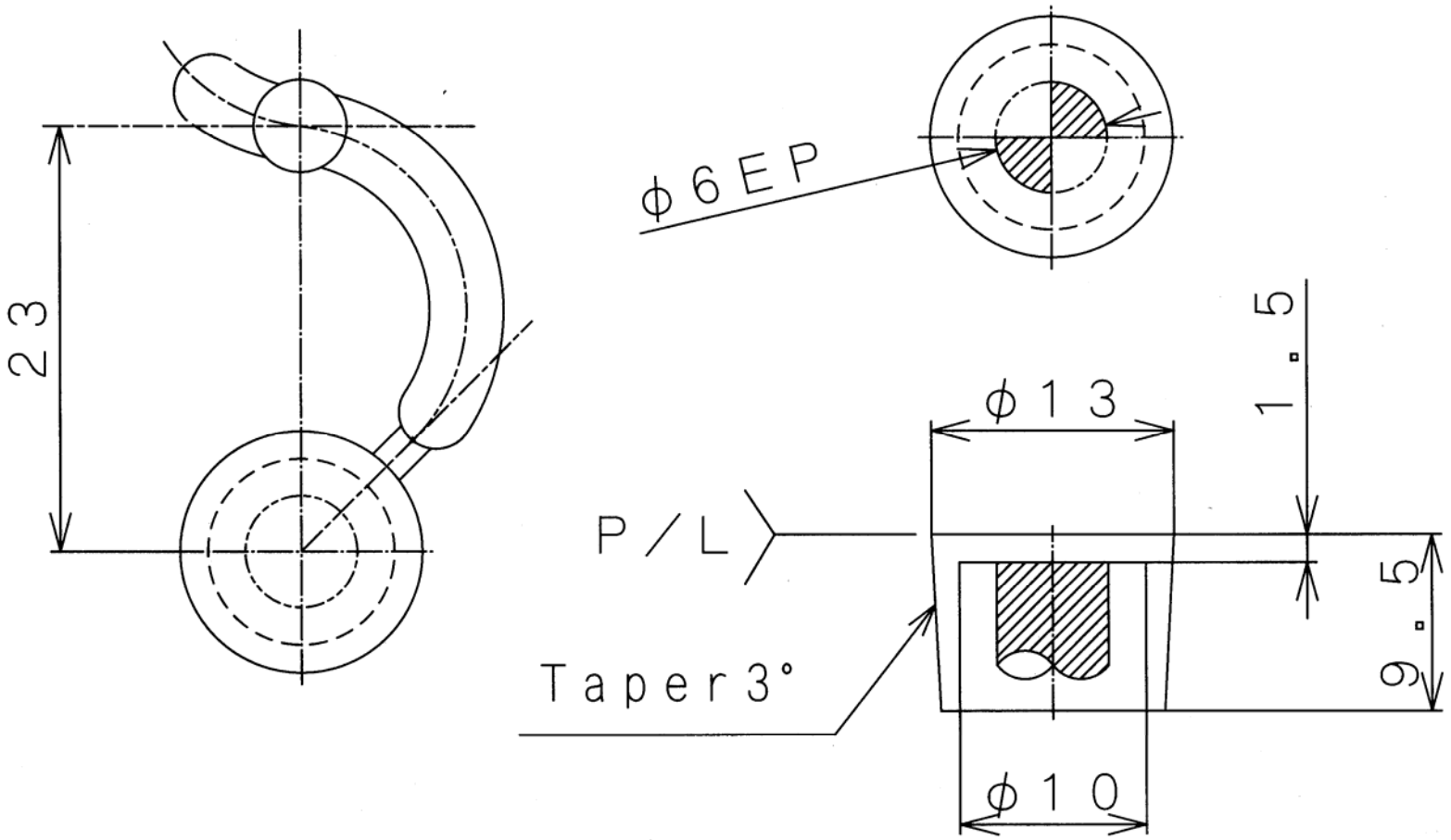

Fig. 1

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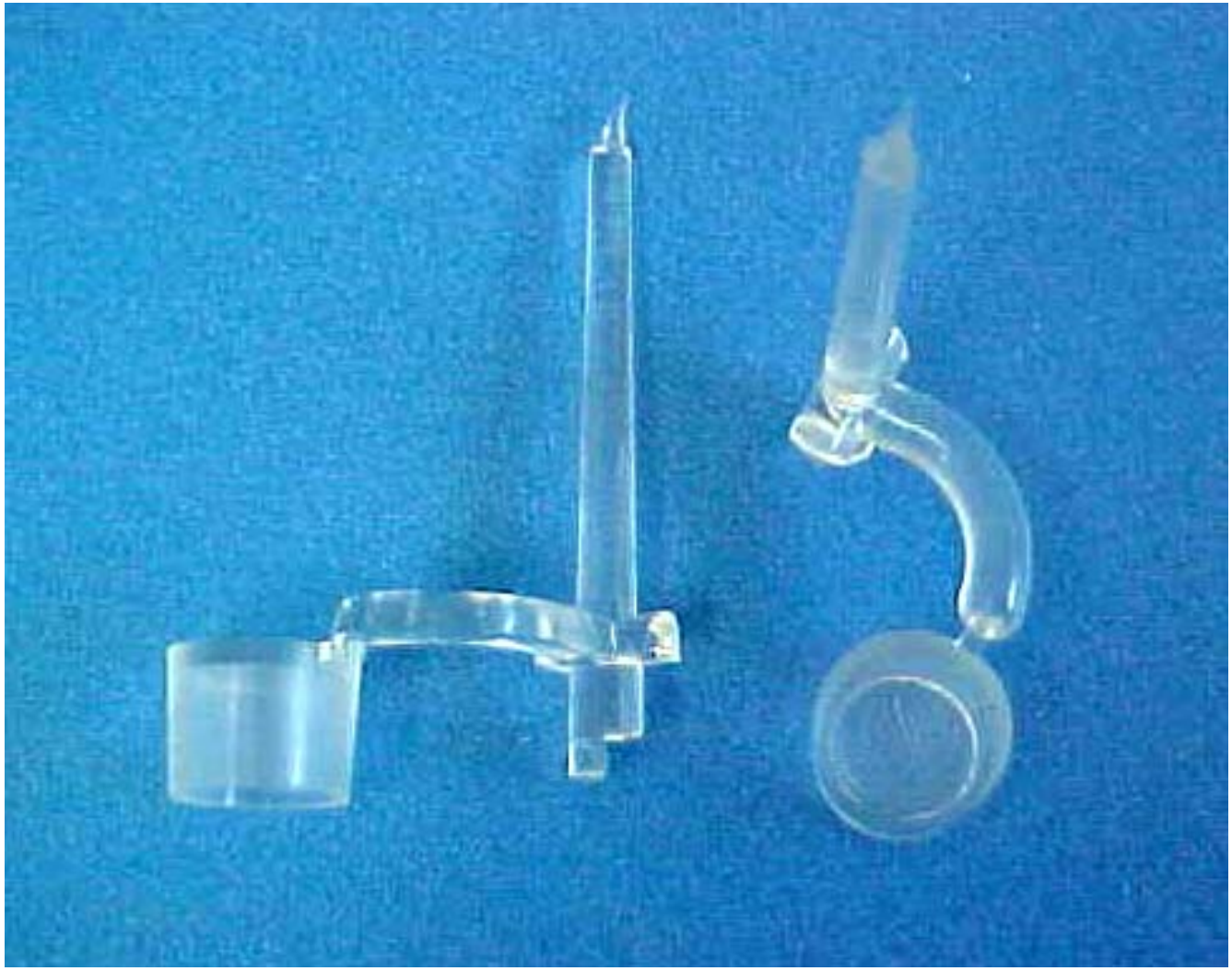

Fig. 2

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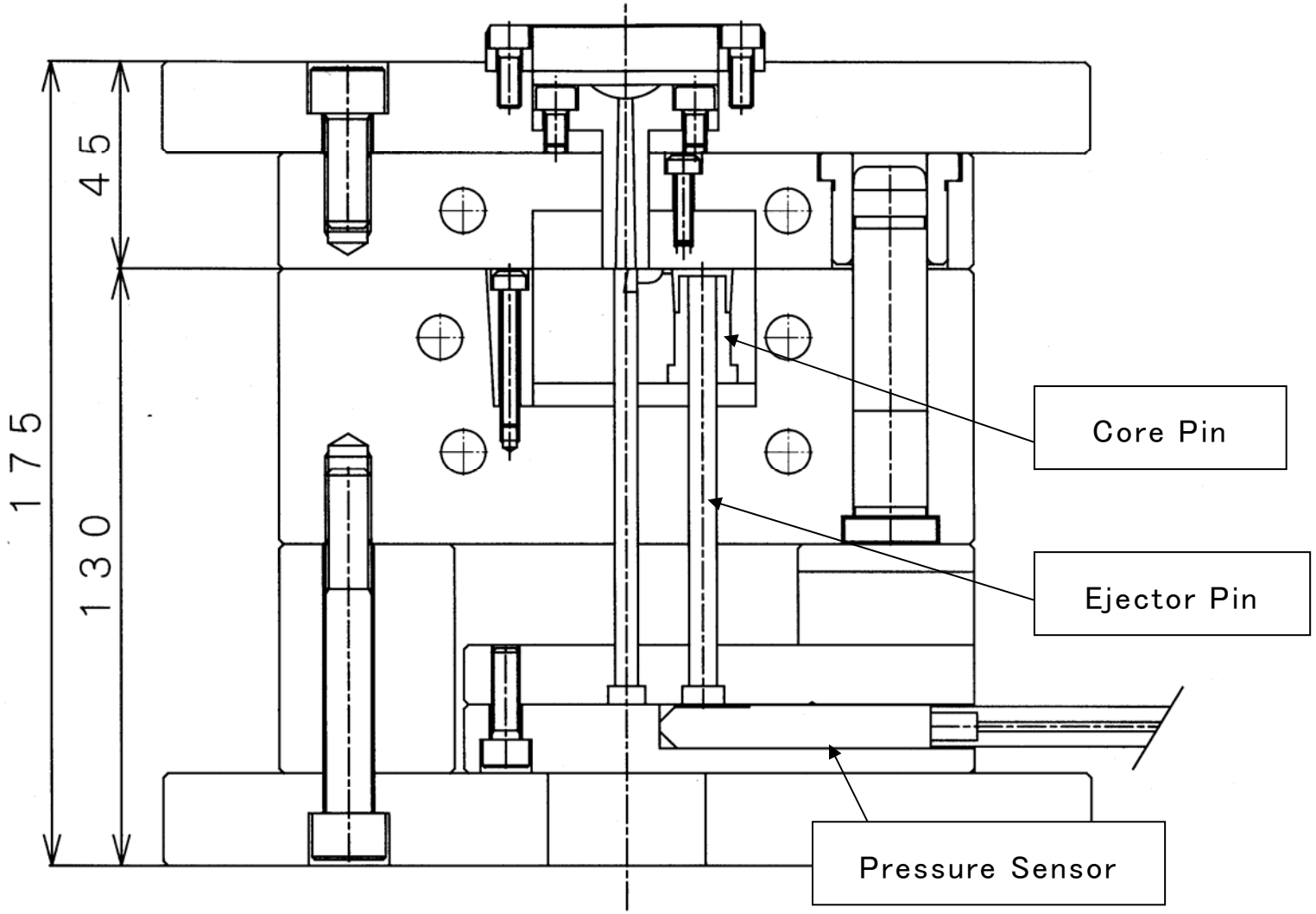

(a)

Fig. 3

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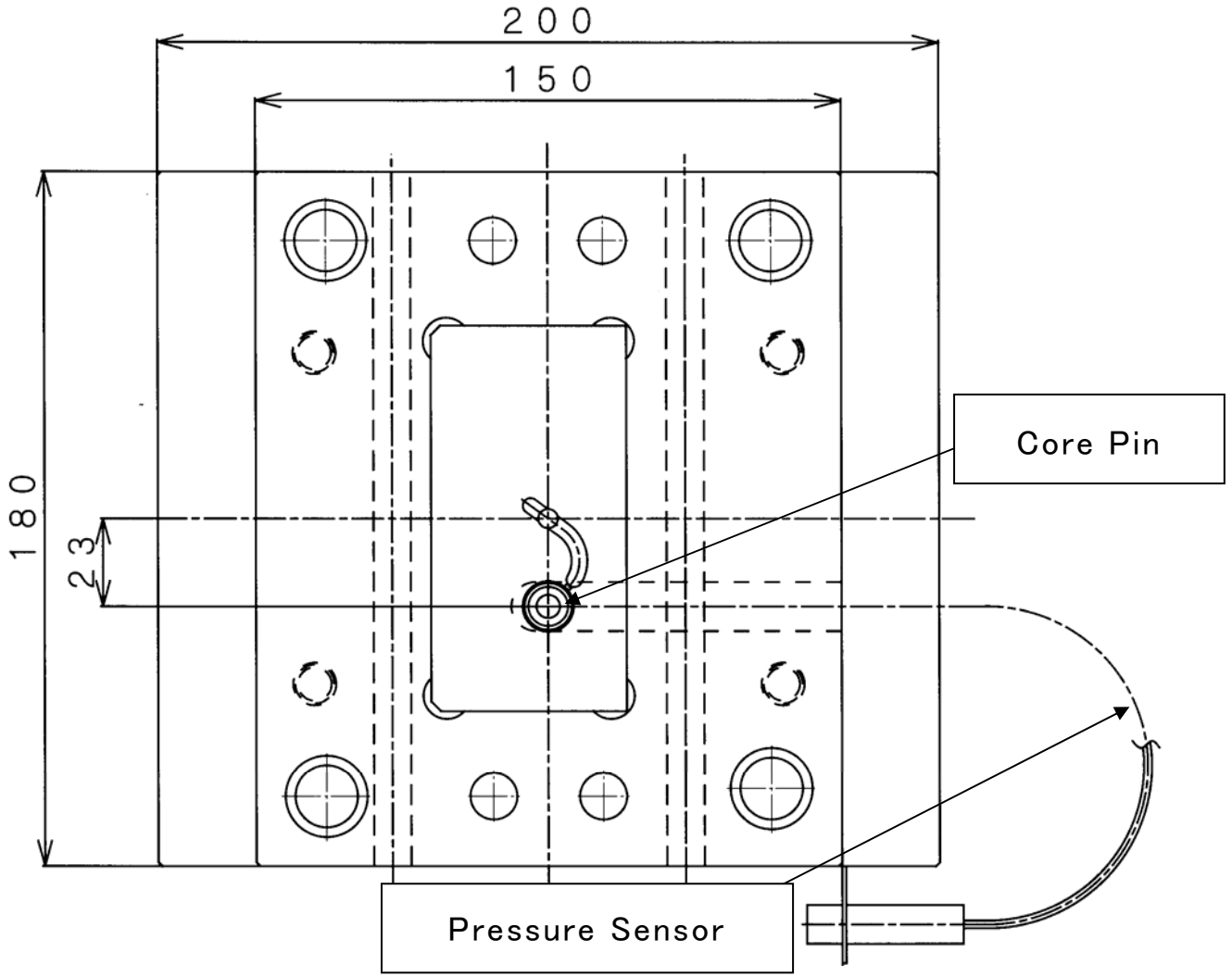

(b)

Fig. 3

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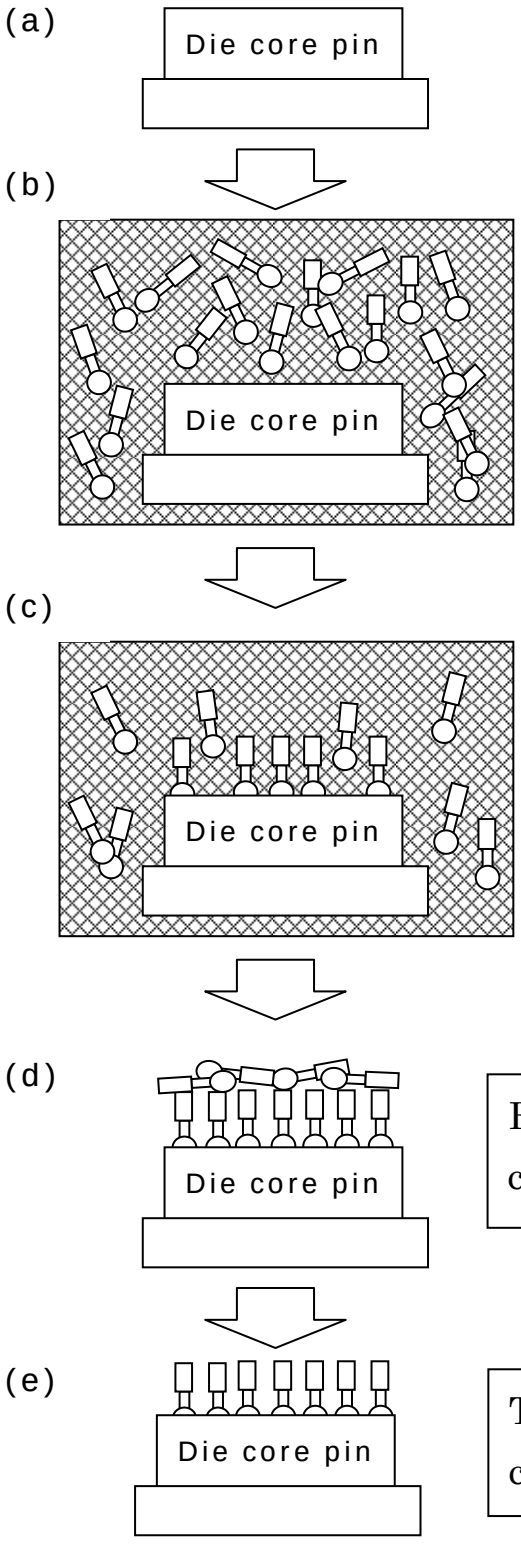

Fig. 4

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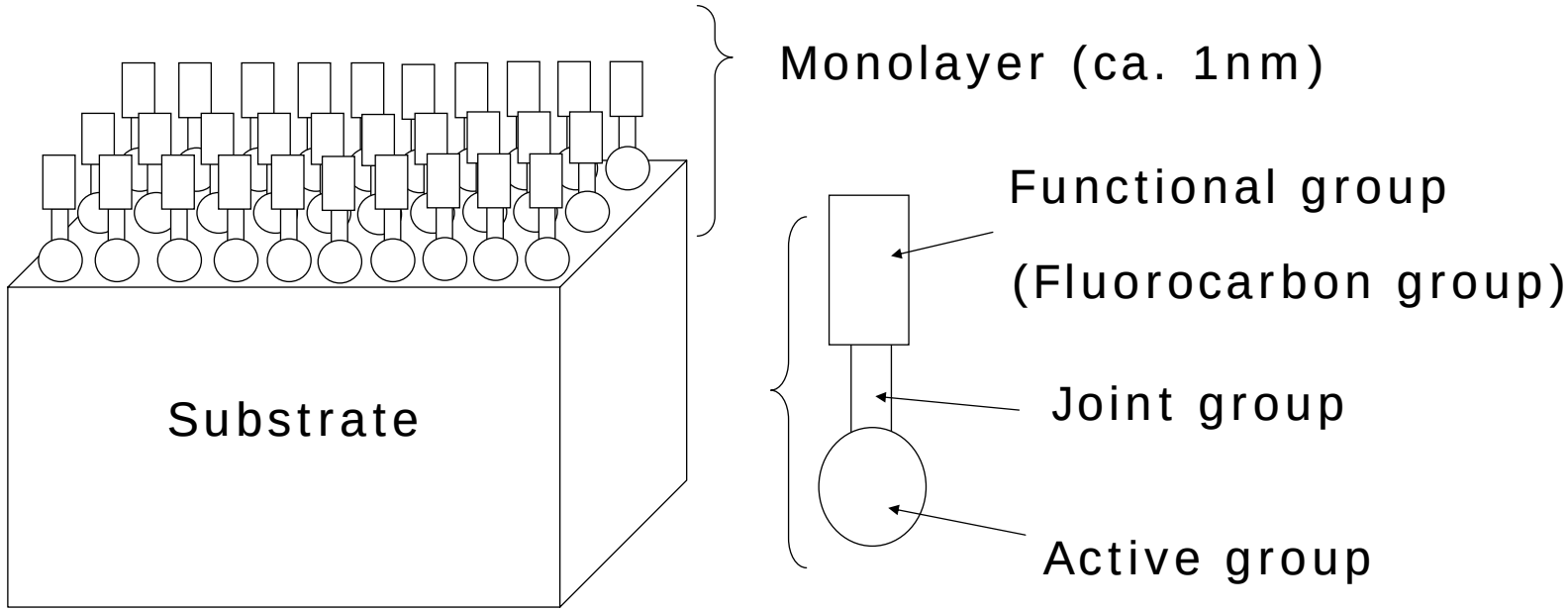

Fig. 5

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Mirror finish

Fig. 6

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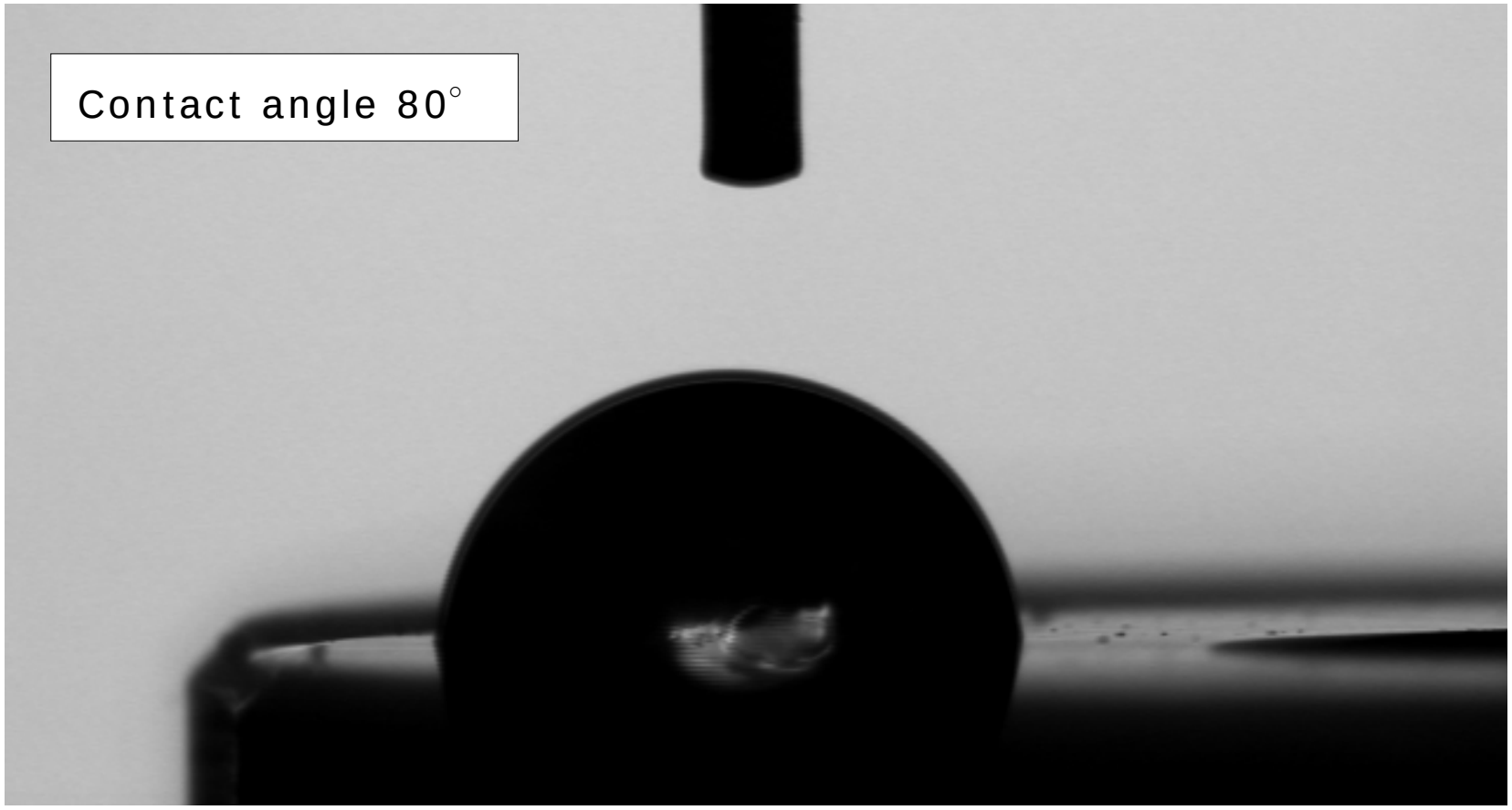

Fig. 7

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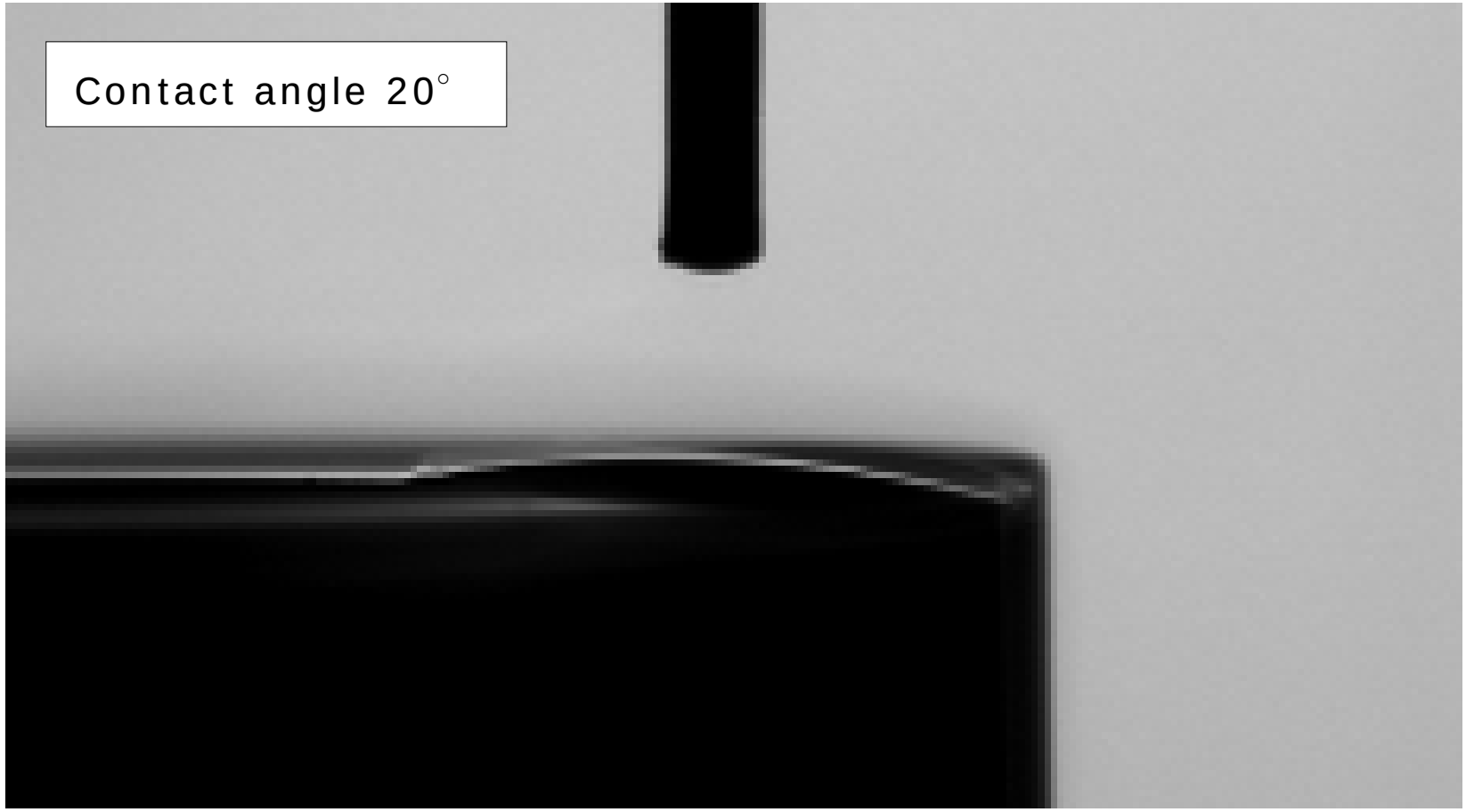

(a)

Fig. 8

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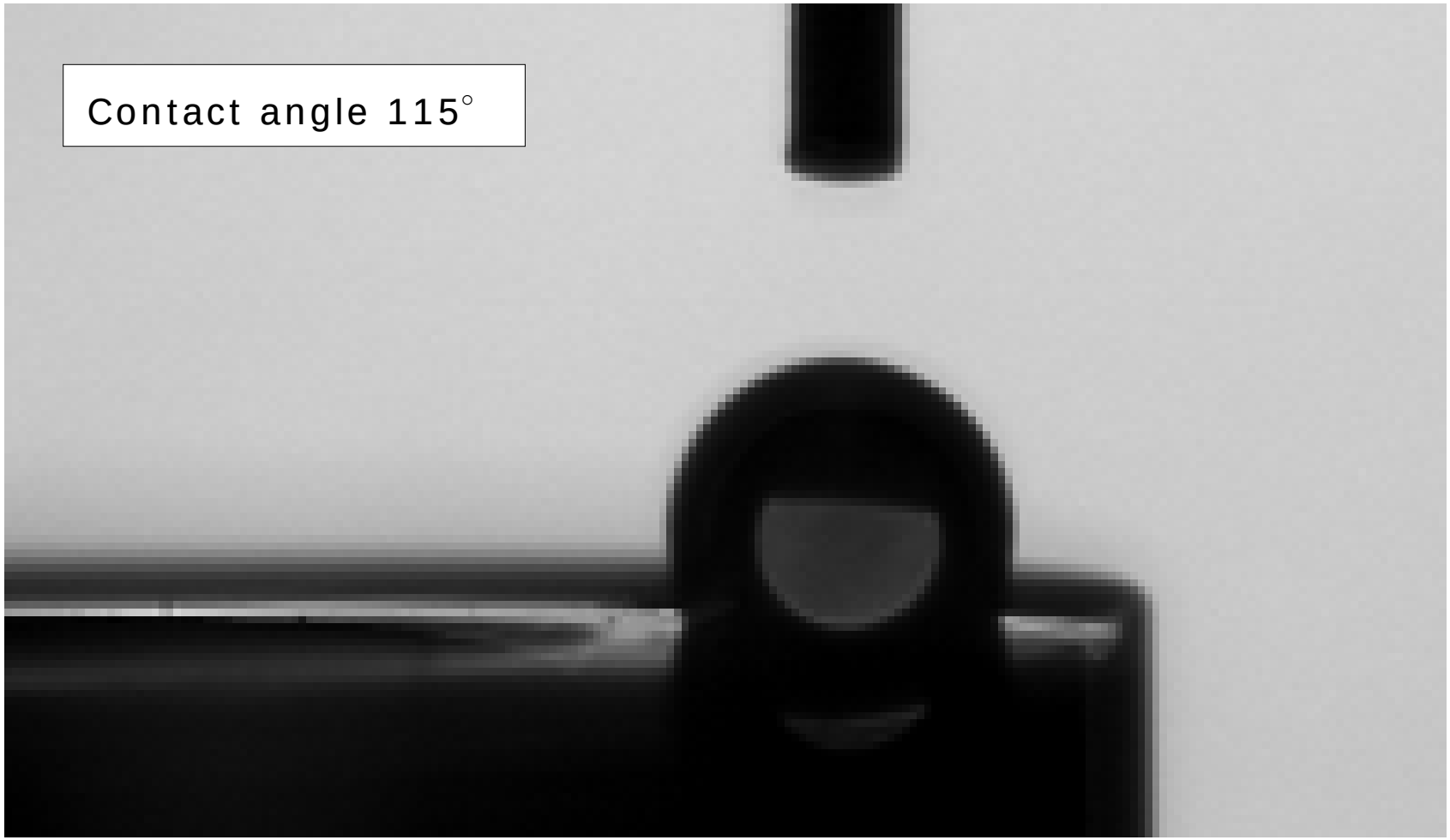

(b)

Fig. 8

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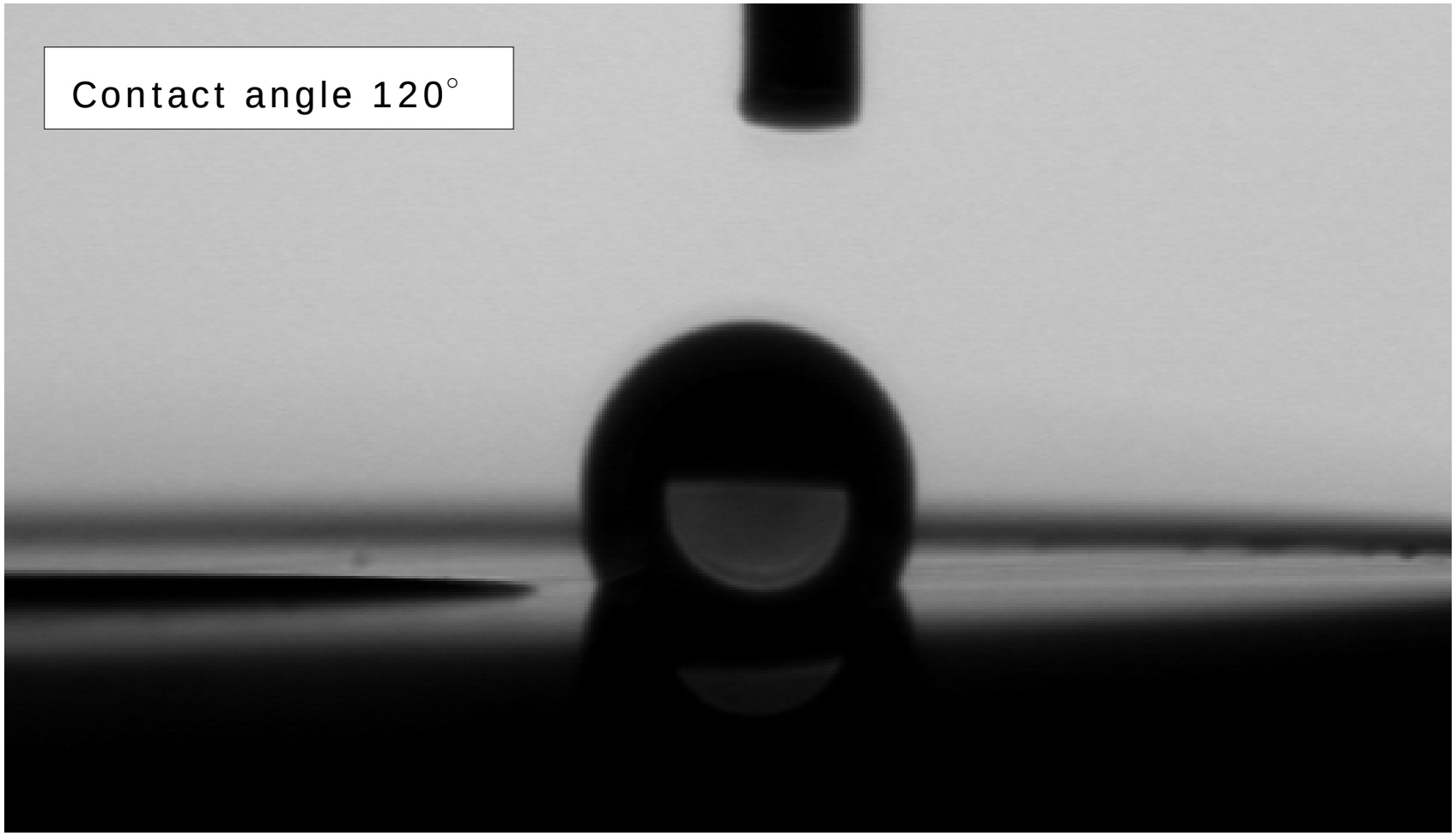

(c)

Fig. 8

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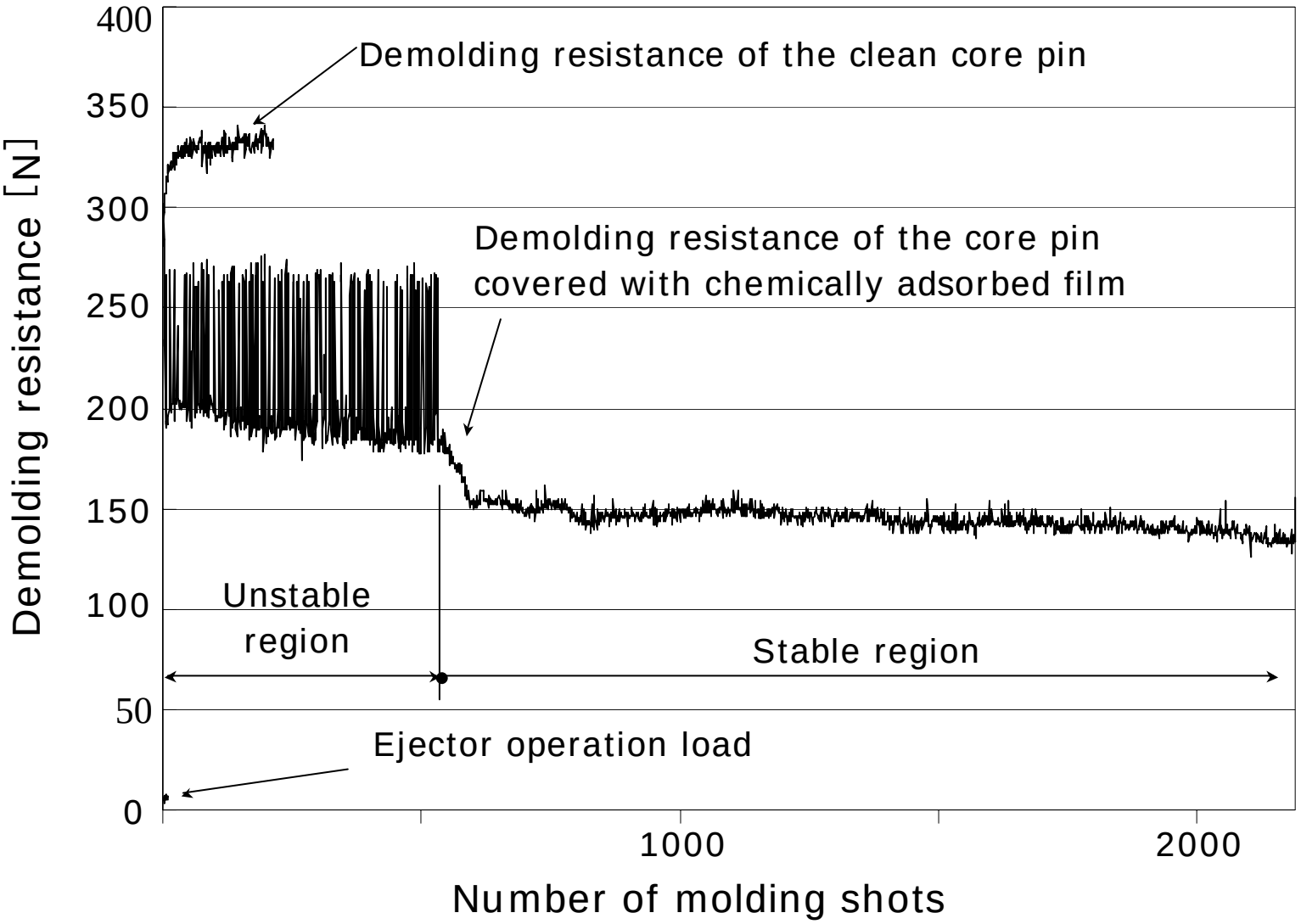

Fig. 9

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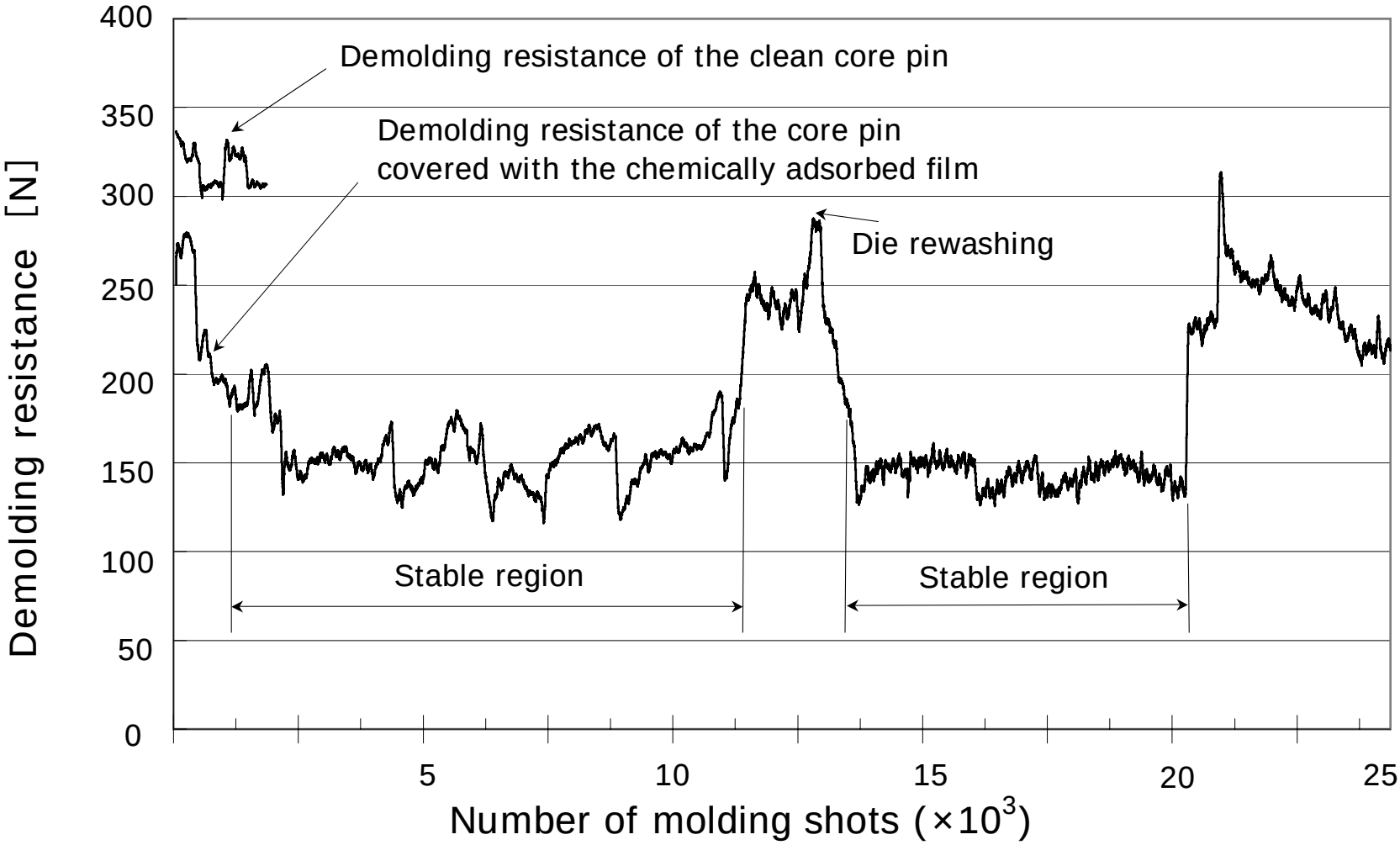

Fig. 10

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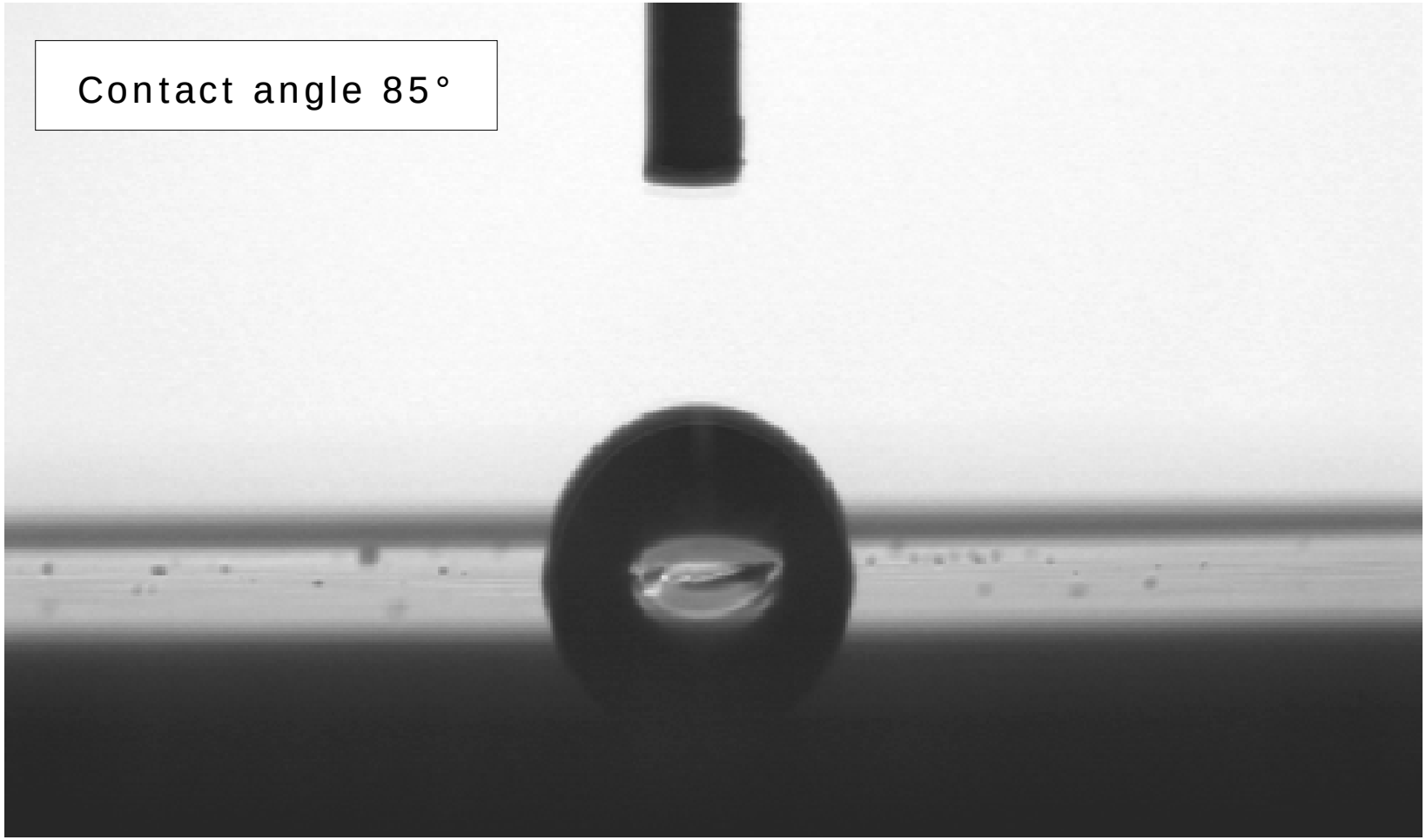

Fig. 11

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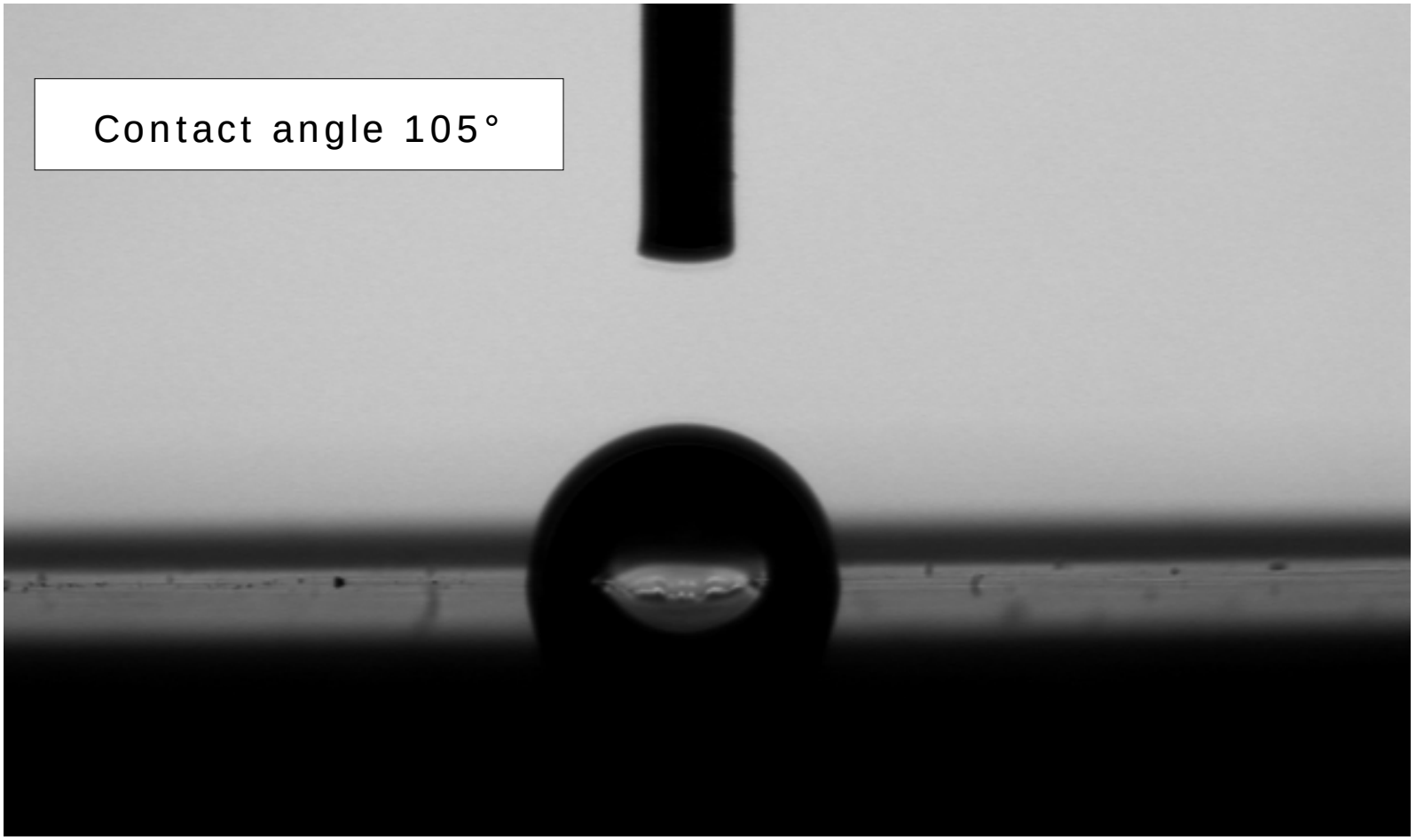

Fig. 12

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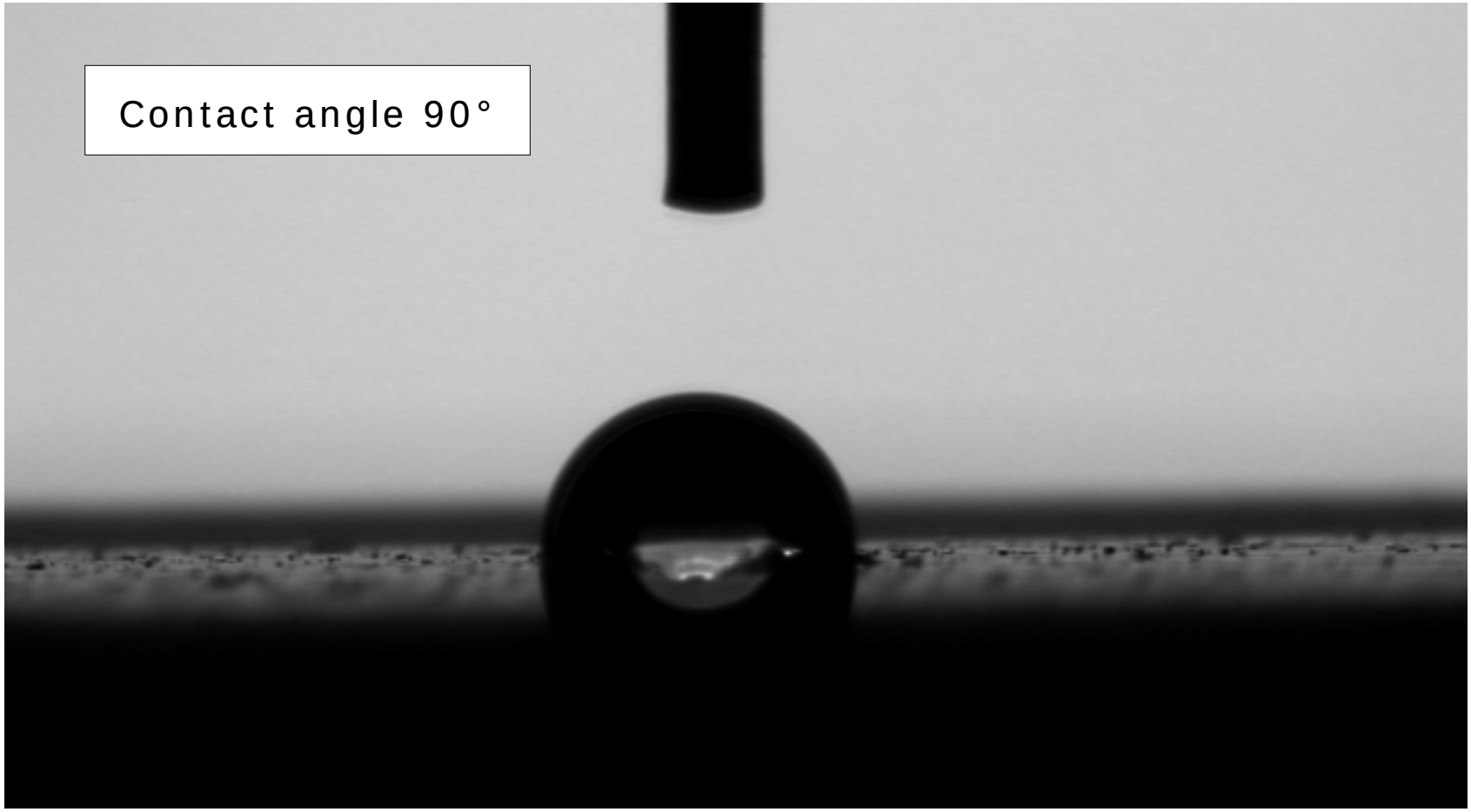

Fig. 13