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MATZDORF et al.

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(54) **CORROSION RESISTANT CHROMIUM
FREE CONVERSION COATINGS**

(71) Applicant: **United States of America as
represented by the Secretary of the
Navy**, Patuxent River, MD (US)

(72) Inventors: **CRAIG MATZDORF**, Hollywood,
MD (US); **Megan Fretz**, Germantown,
MD (US); **Joshua Walles**, California,
MD (US)

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(57) **ABSTRACT**

Process for treating metal such as aluminum and its alloys to prevent corrosion which comprises coating the metal with a chromium-free conversion composition containing effective amounts of metal fluorozirconates and carboxylic metal salts.

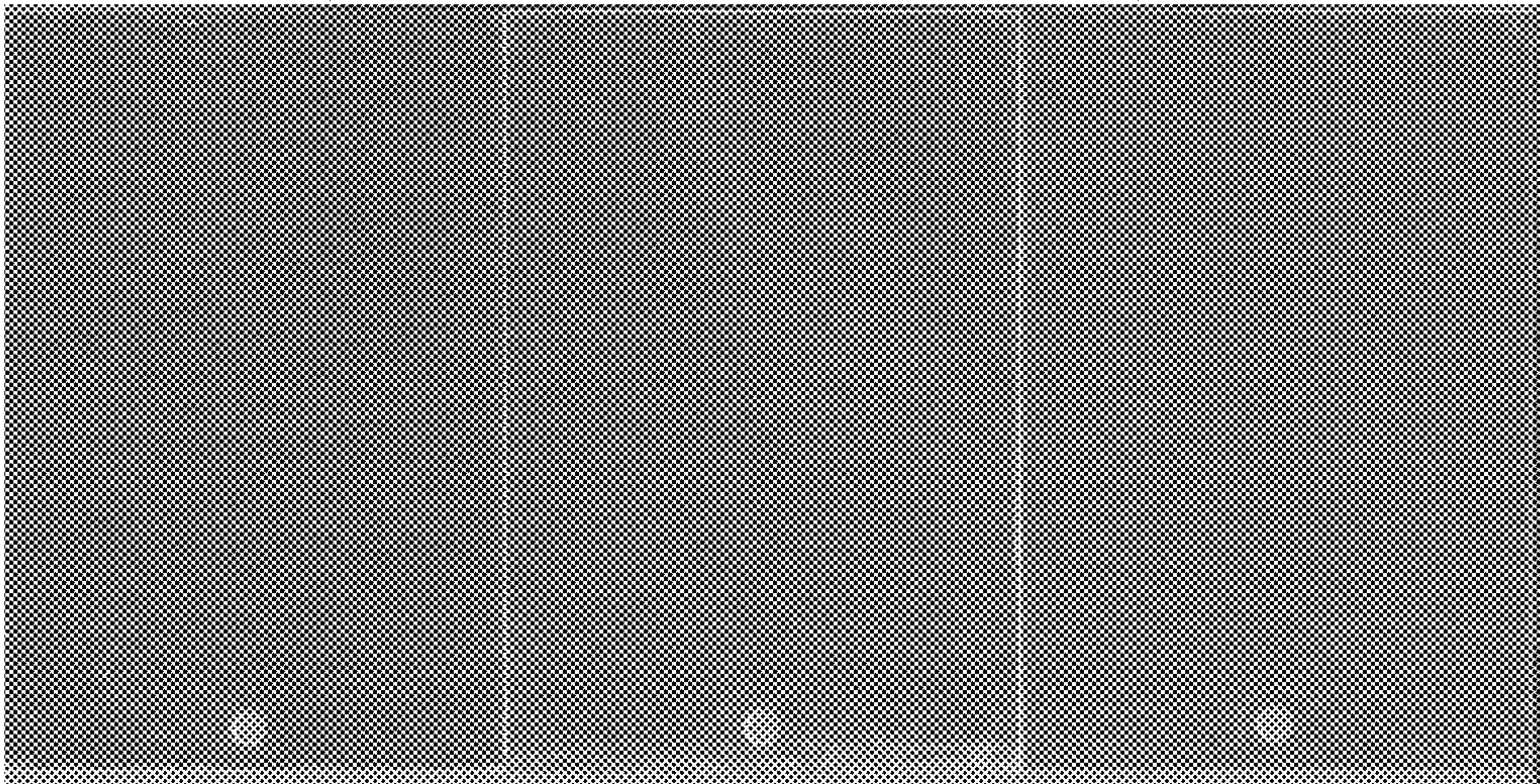


Figure 1a

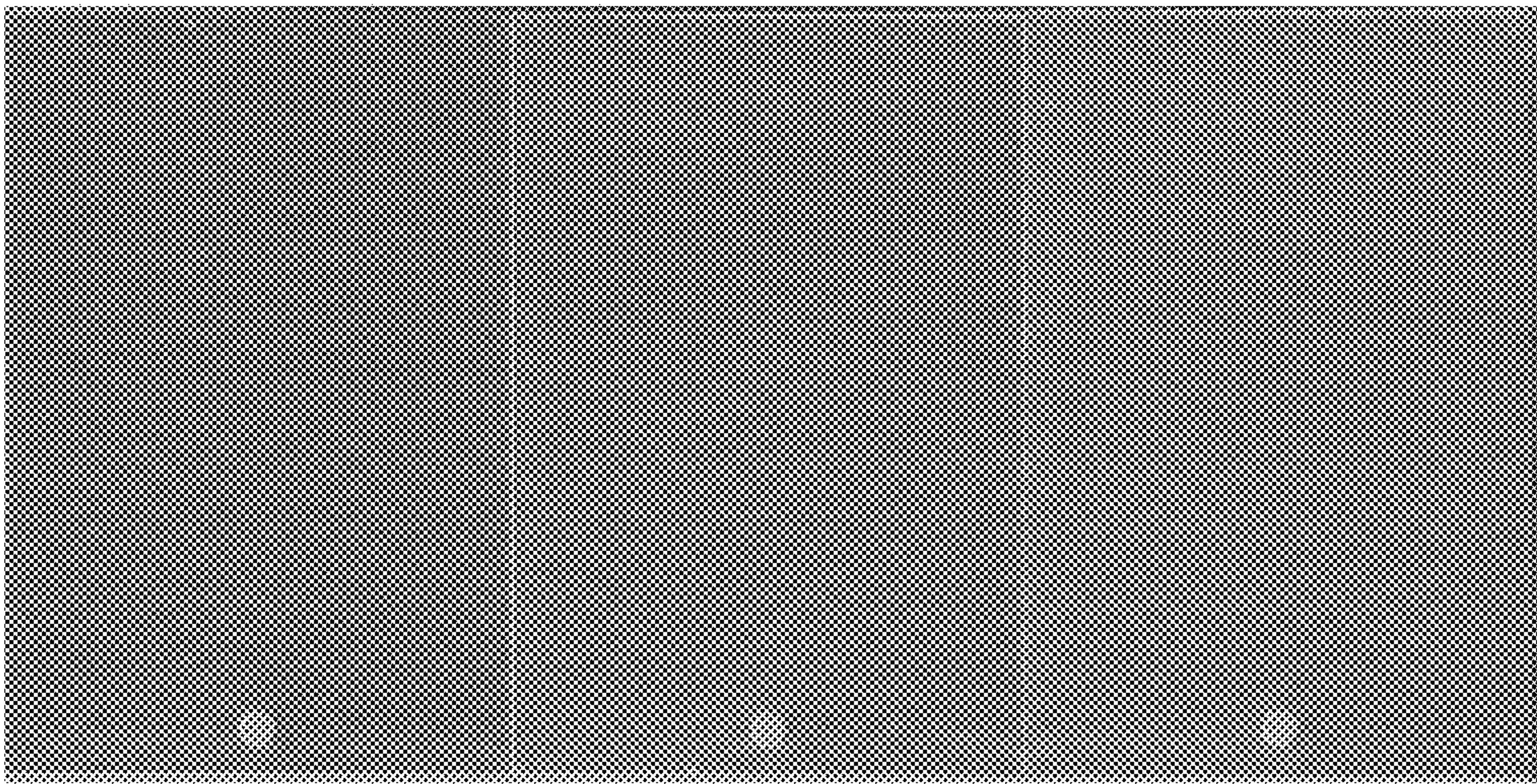


Figure 1b

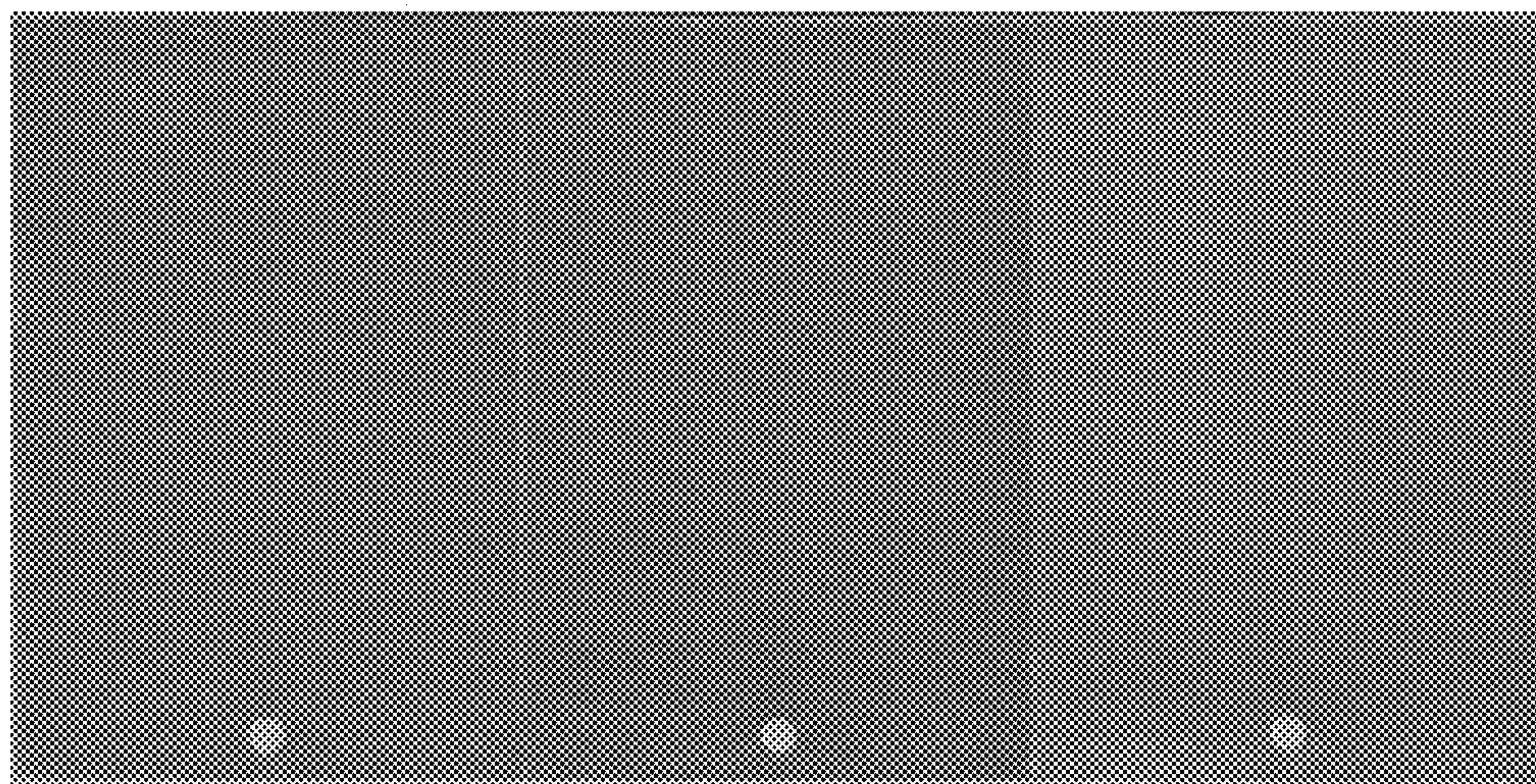


Figure 1c

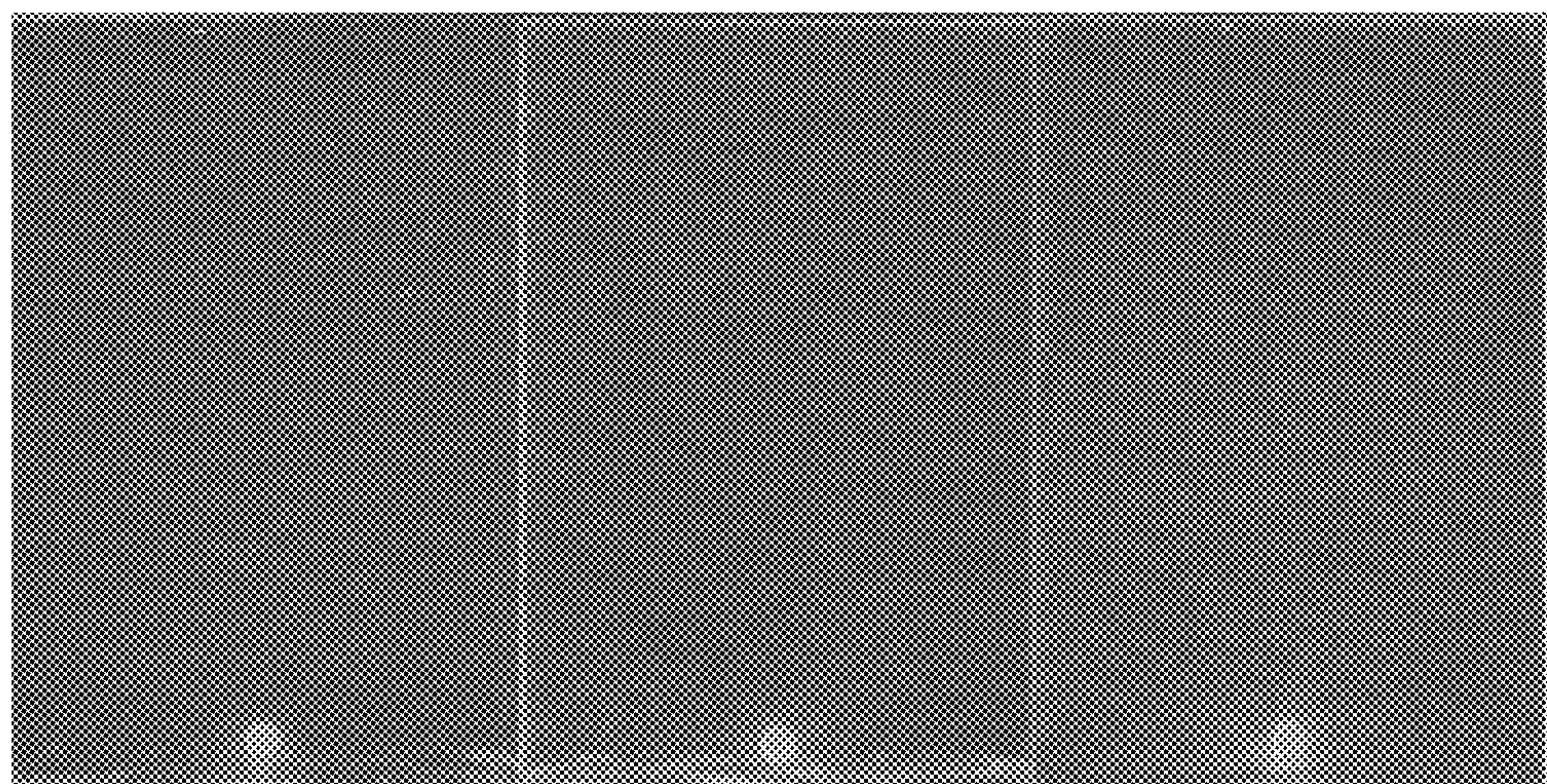


Figure 1d

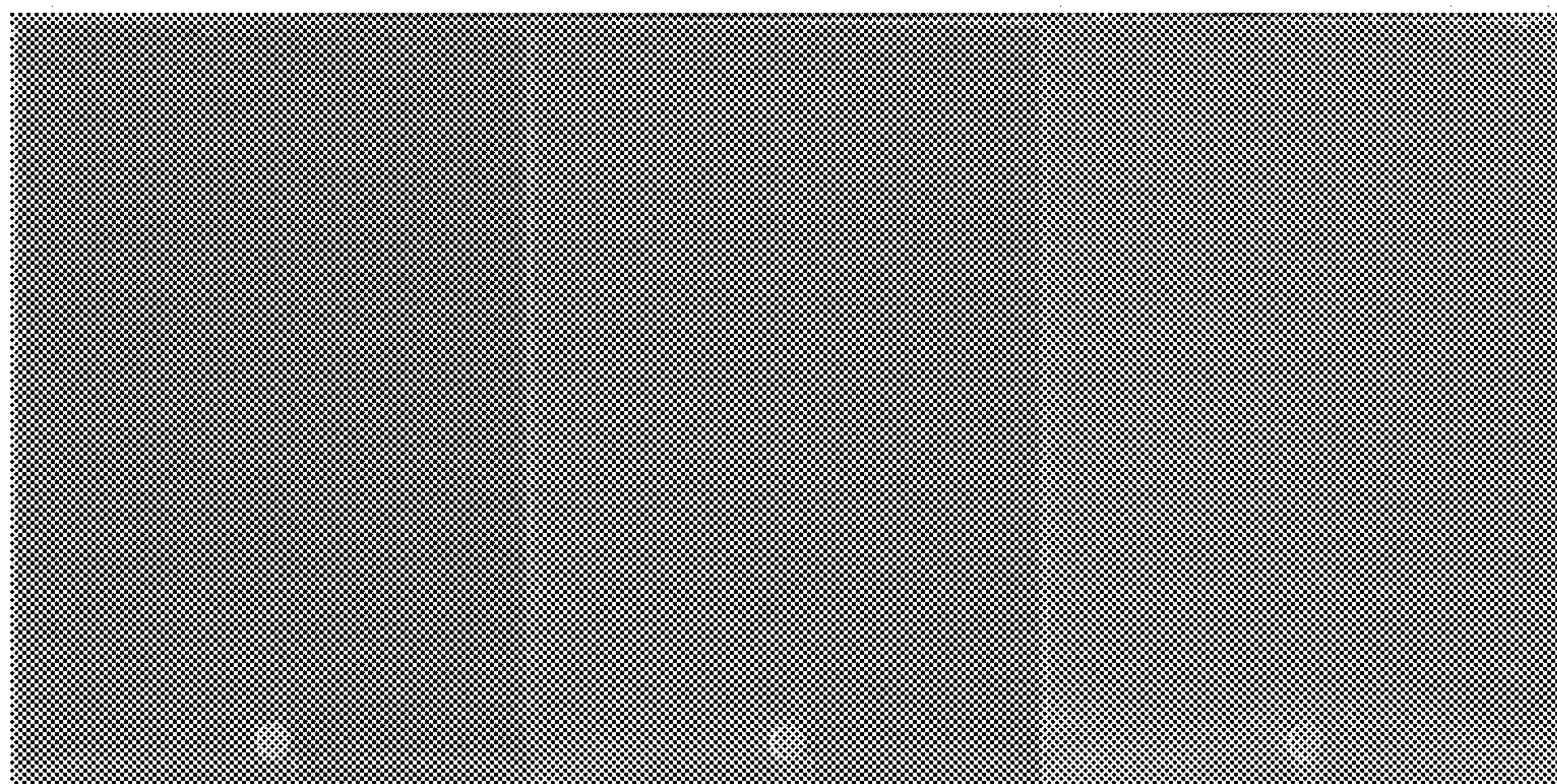


Figure 1e



Figure 2a

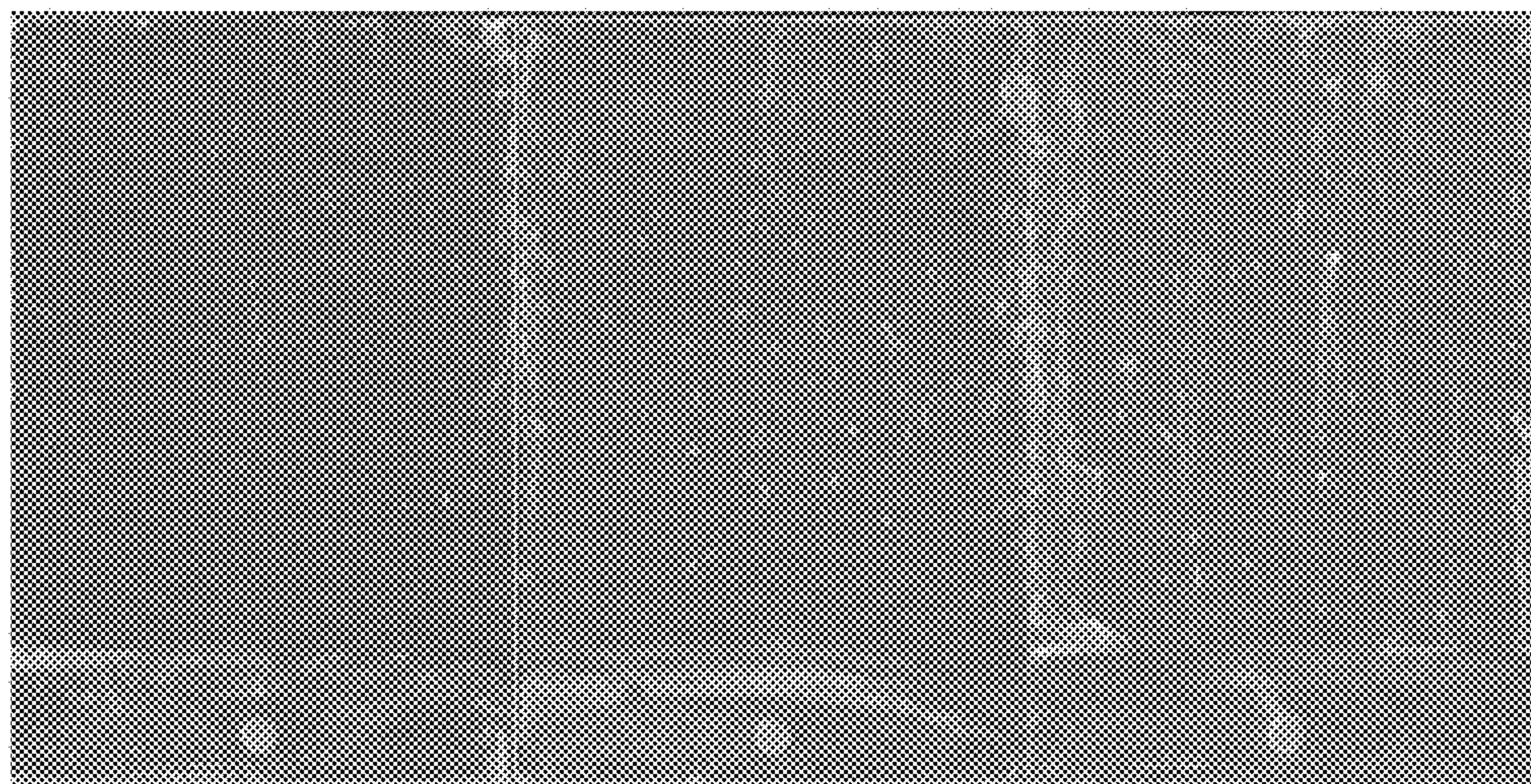


Figure 2b

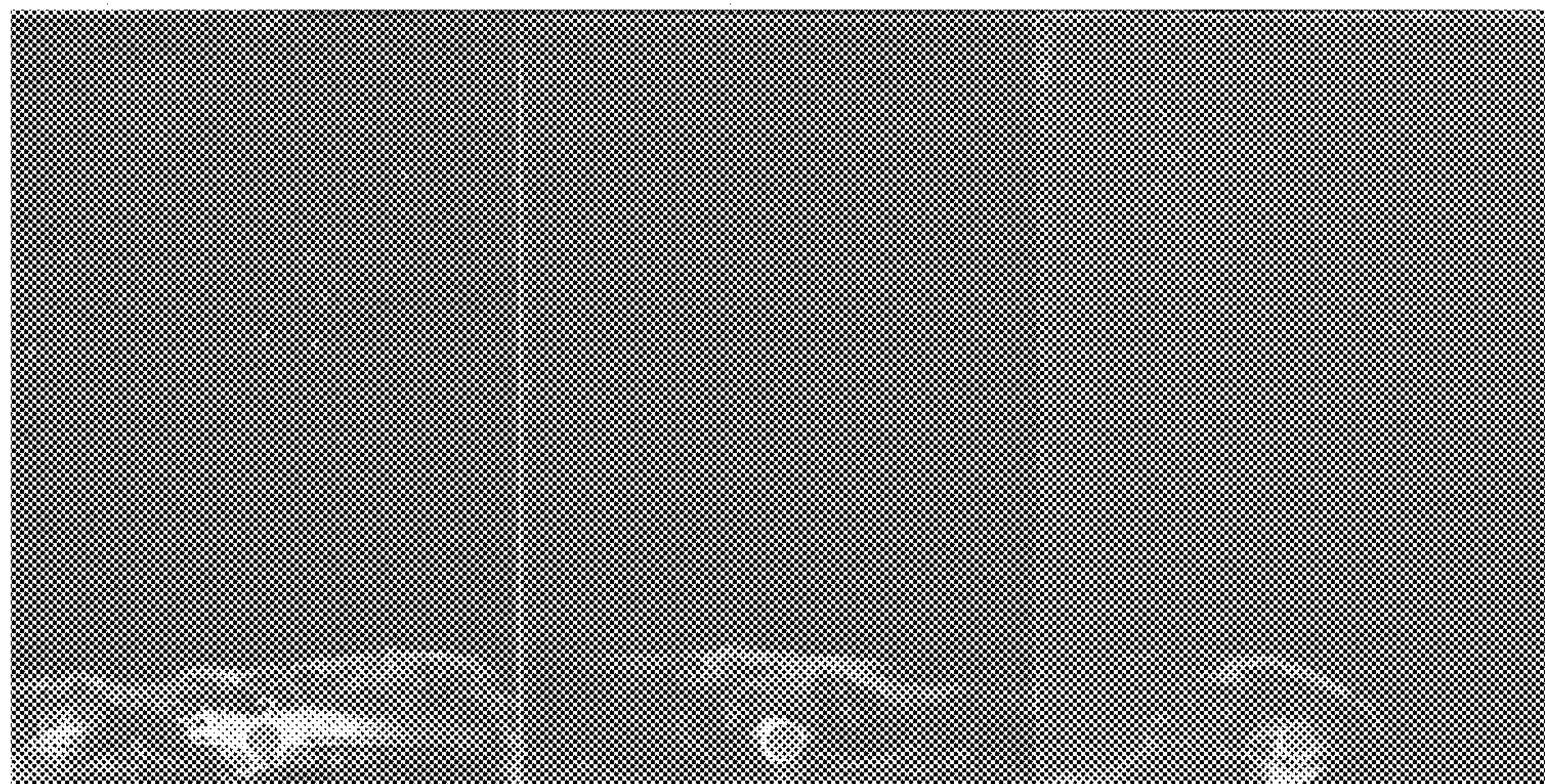


Figure 2c



Figure 2d

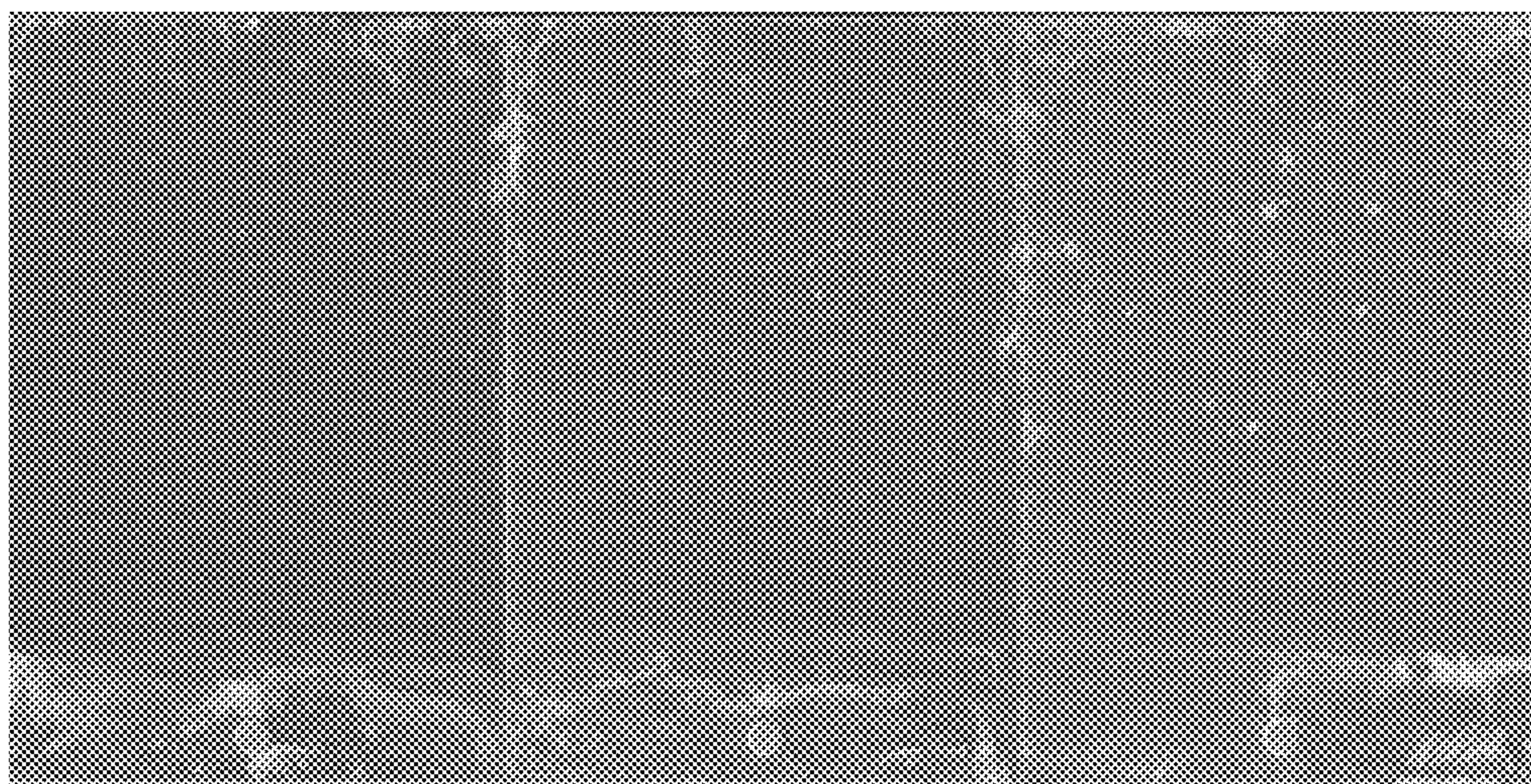


Figure 2e

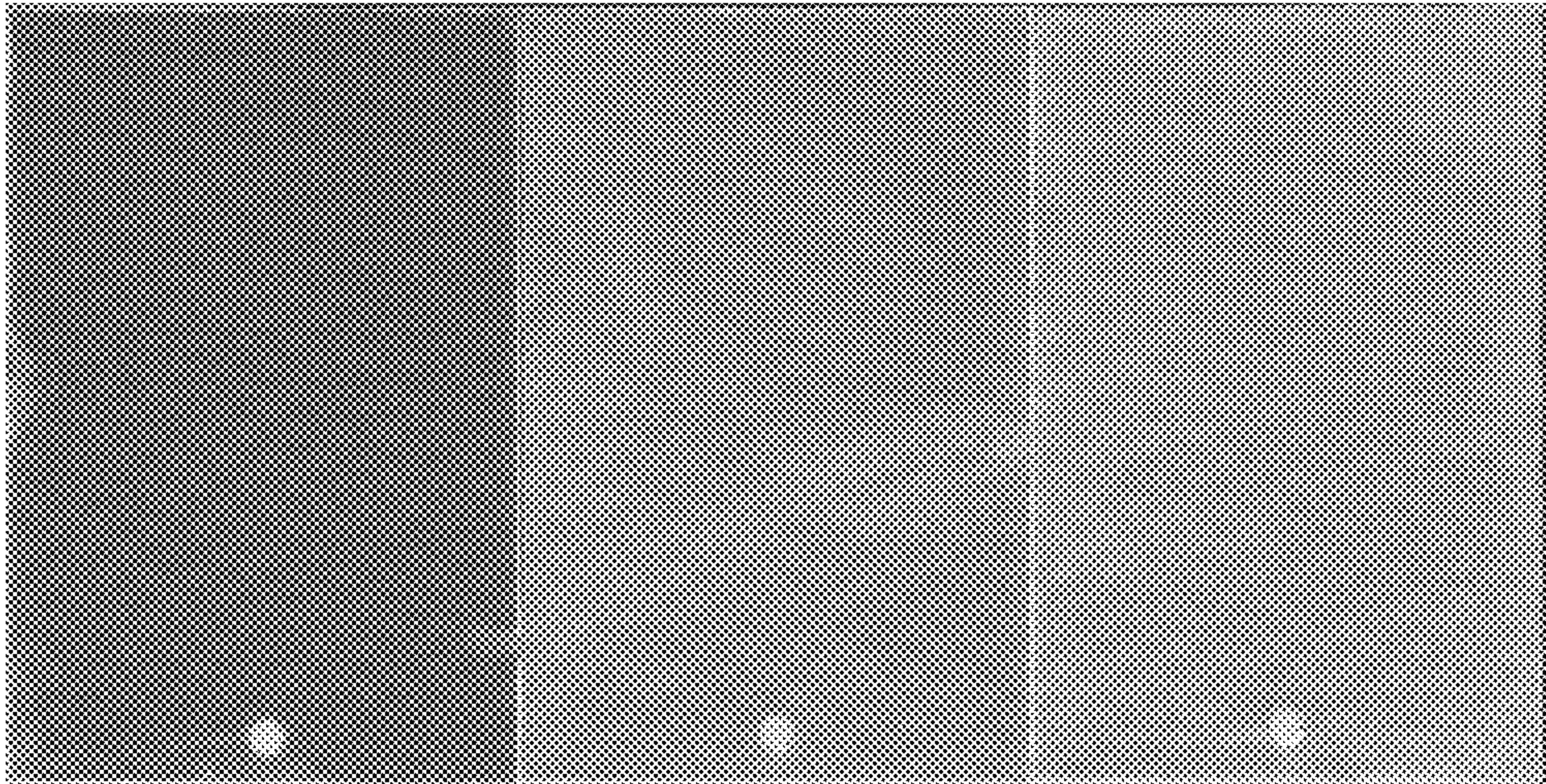


Figure 3a

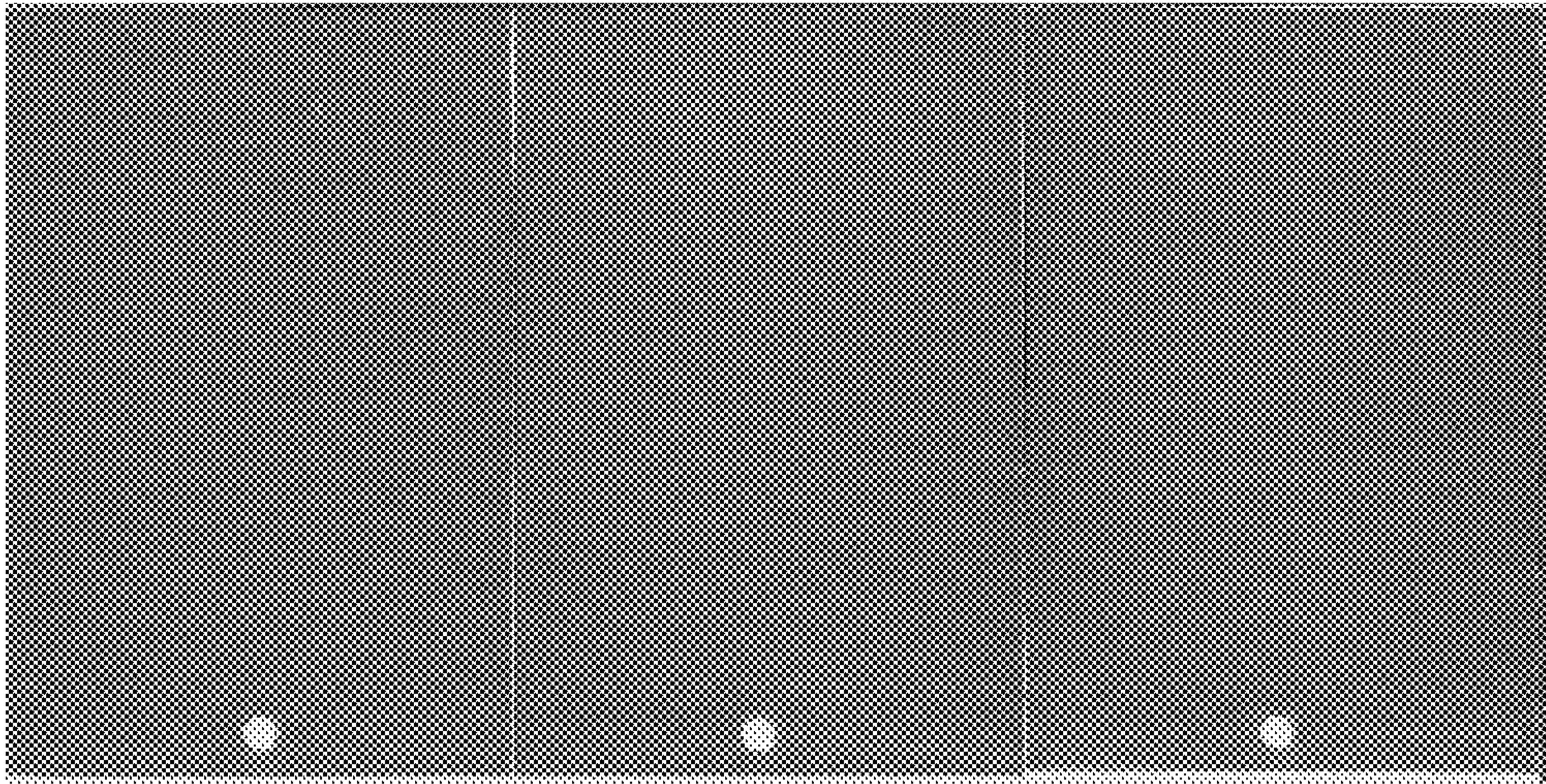


Figure 3b

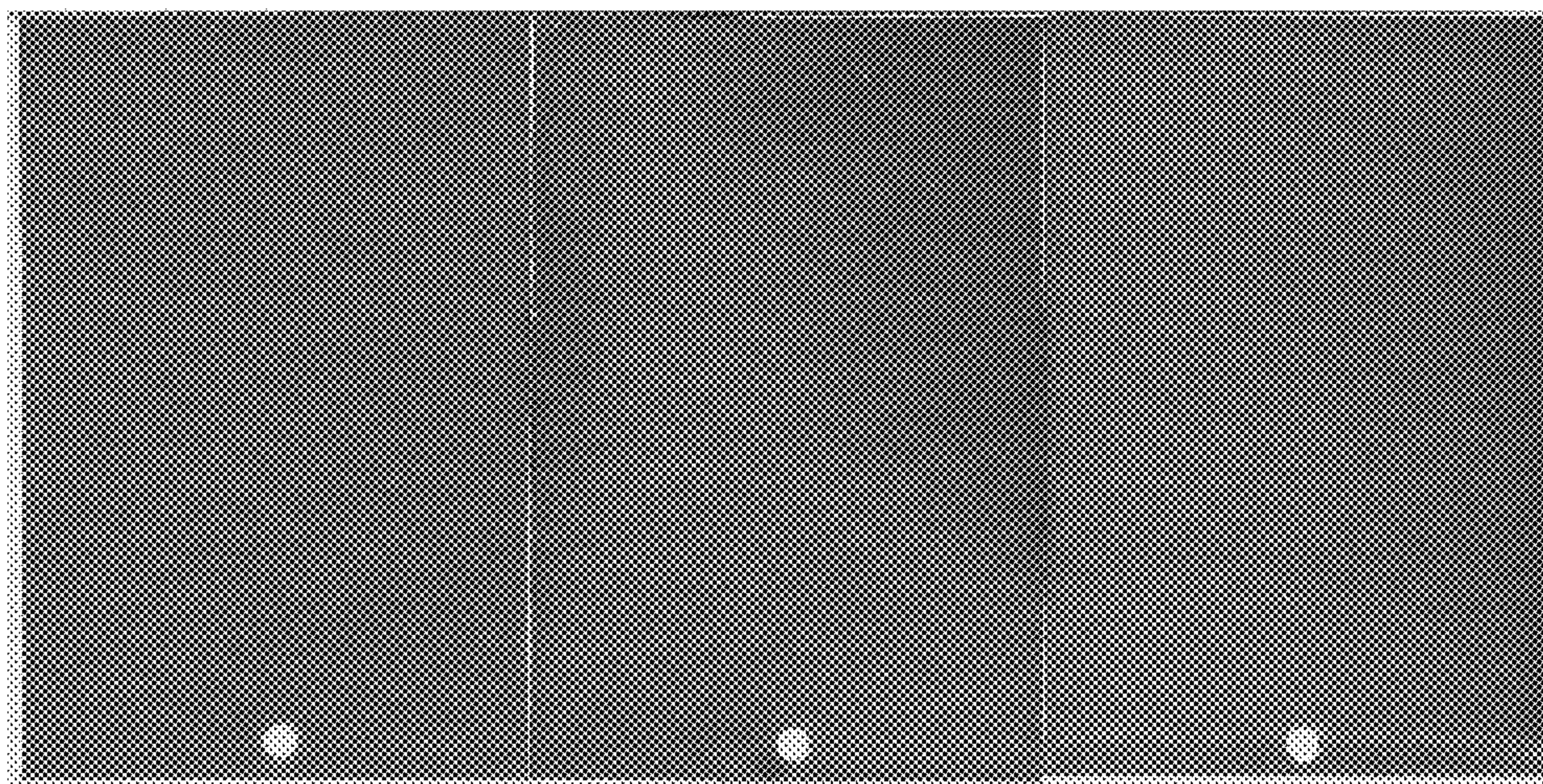


Figure 3c

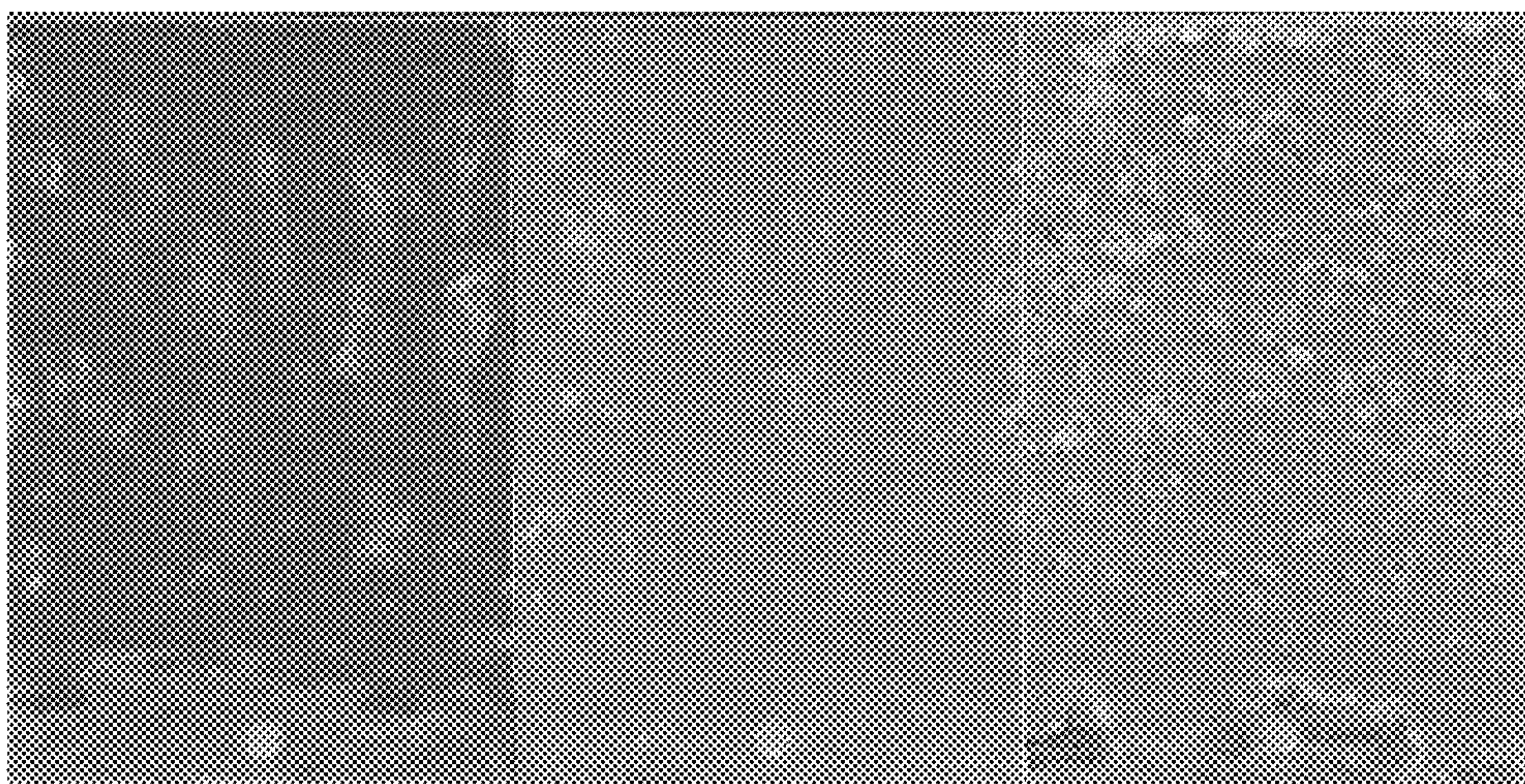


Figure 4a

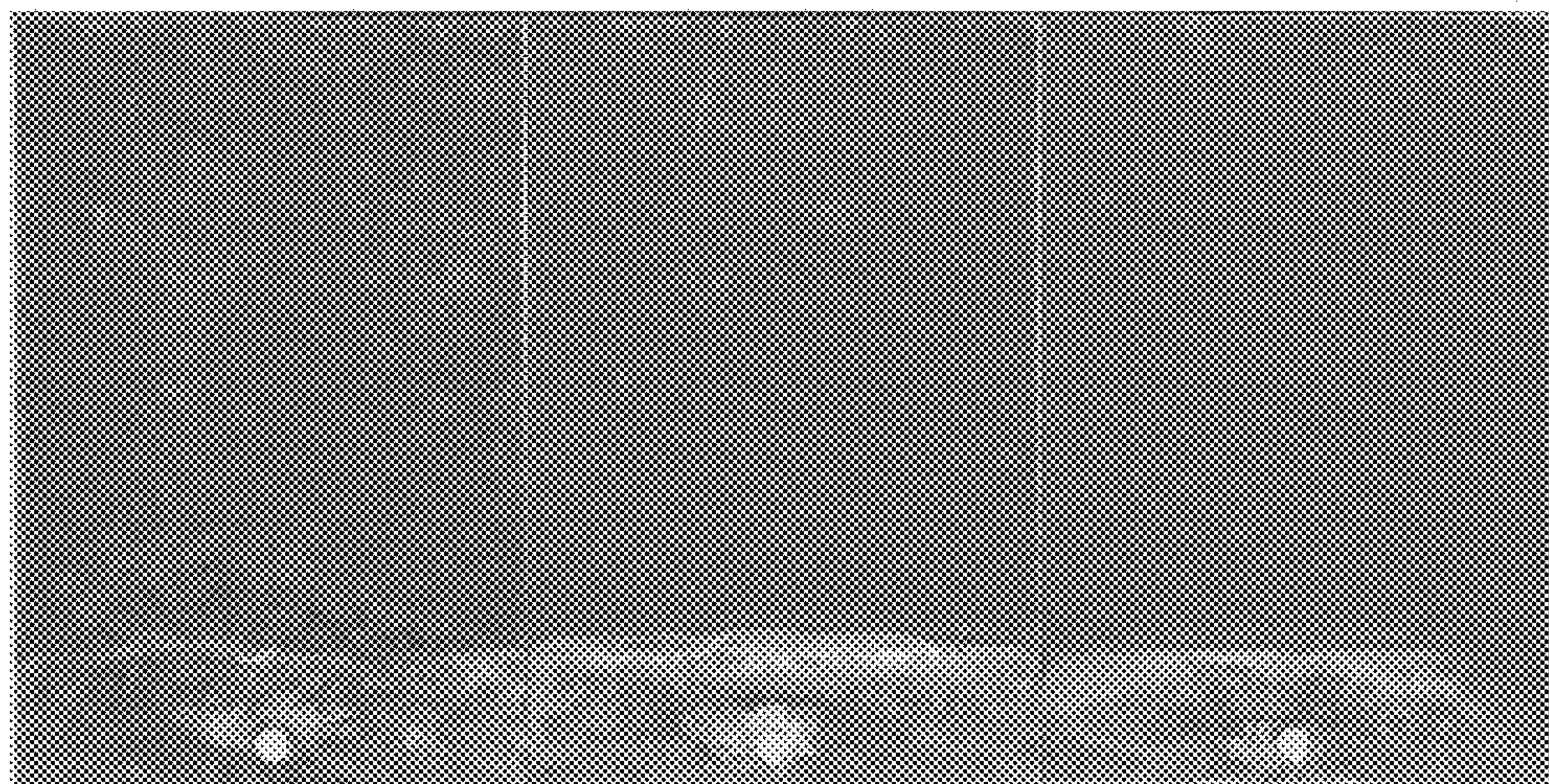


Figure 4b

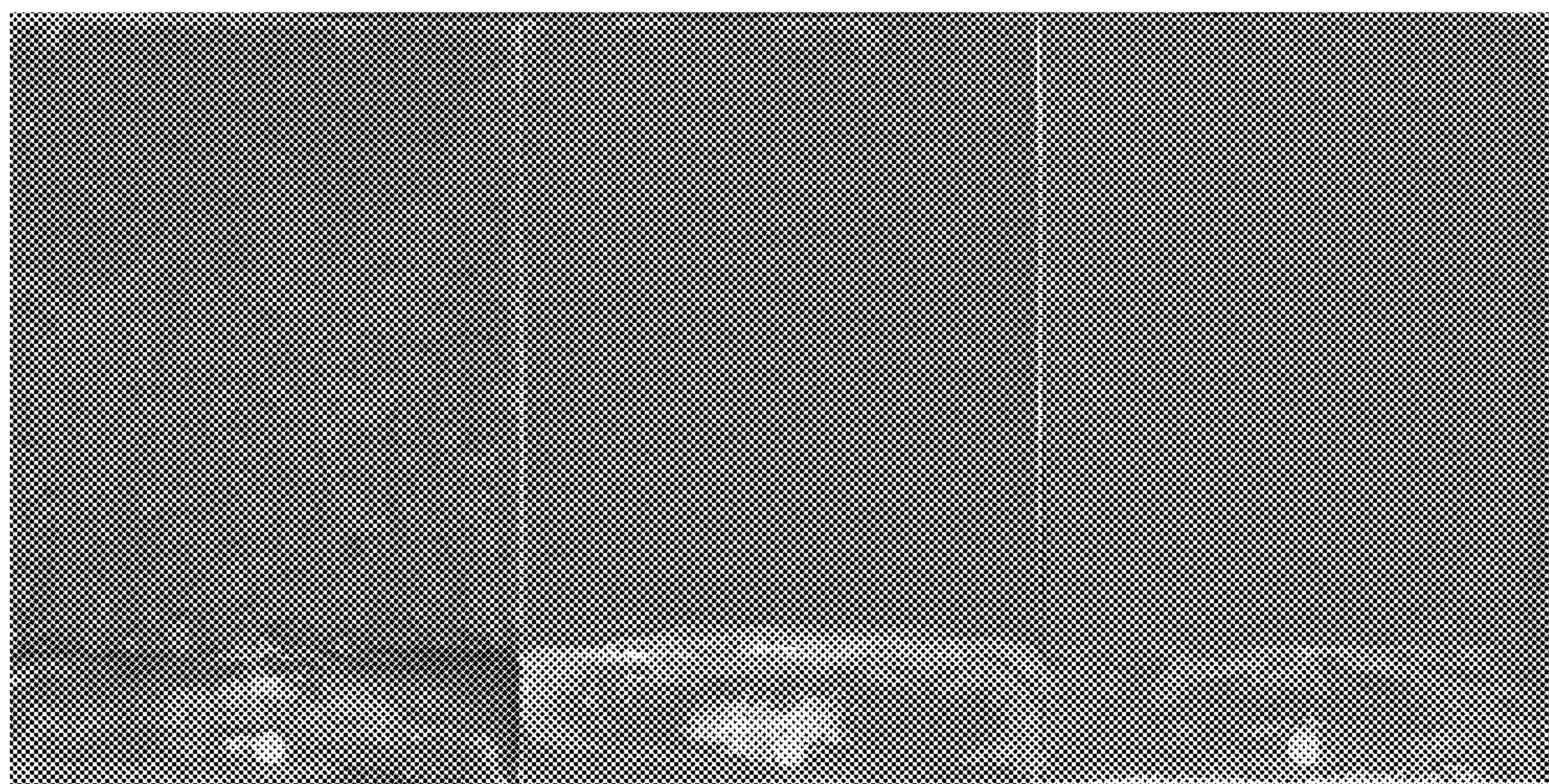


Figure 4c

CORROSION RESISTANT CHROMIUM FREE CONVERSION COATINGS

ORIGIN OF INVENTION

[0001] The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

FIELD OF THE INVENTION

[0002] The invention constitutes the incorporation of corrosion inhibitor salts with at least one carboxylate anion and a variety of cations in conversion coatings for aluminum and aluminum alloys to enhance corrosion performance and paint adhesion. The inhibitor salts improve the corrosion resistance of these conversion coatings to a degree in which a chromium free conversion coating has the potential of meeting military specifications.

[0003] Carboxylate salts with varying cations and anions have been evaluated in aluminum rich primers, proving to be effective at increasing corrosion resistance of the non-chromate primer. Additional research has been done in testing these inhibitors in aqueous solutions in an effort to increase corrosion performance of non-chromium conversion coatings. While salts with organic anions tend to incorporate well in organic primers, data suggests the salts in aqueous solutions provide a different mechanism in which they are providing corrosion resistance. Unlike paint systems, the quality of coatings formed by immersion in conversion coating is dependent on the substrates' surface properties and the chemistries within the bath, leading to greater variability.

[0004] The novel features of these inhibitor salts are their carboxylate anions, which result in varying water solubility and therefore, seemingly altering the mechanism in which the coating is formed on the metallic substrate. Typical corrosion inhibitors will dissociate in solution and react with the metal substrate or bind to the primitive layers of the coatings. However, the low solubility of these salts and as analytical data indicates the salts may not deposit on the metal substrate in this manner.

BACKGROUND

[0005] Prior conversion coatings have used soluble inorganic salts as inhibitors but none so far have incorporated carboxylate salts. Due to the believed mechanism of conversion coating formation, it is not intuitive that insoluble or very slightly soluble compounds would outperform salts with the same cations with high solubility. Despite the developments of the prior art, the corrosion resistance by non-chromate treatments is less than that provided by chromate methods, particularly in the aircraft industries. This invention relates to chromium free coatings which are capable of providing corrosion protection similar to a chromium coating.

[0006] For decades, hexavalent chromium (Cr6+) compounds, such as sodium dichromate, have been used as corrosion inhibitors in surface finishing treatments on metallic substrates. Specifically, aluminum and aluminum alloys are often treated with Cr6+-based conversion coatings to increase corrosion resistance and promote paint adhesion to the base substrate. However, entities have established Cr6+

compounds as being harmful to the environment and health, and to comply with the growing amount of regulations, efforts to reduce and replace hexavalent chromium in conversion coatings are increasing.

[0007] In response to the need to eliminate the use of Cr6+, NAWCAD developed TCP technology (trivalent chromium process), based on trivalent chromium (Cr3+). TCP has been successfully transitioned for many uses that were previously based on Cr6+. However, some users are pursuing total chromium-free metal finishing to more effectively comply with water treatment and other compliance regulations. Due to the demand for chromium-free conversion coatings many surface finishing companies are developing non-chromium conversion coatings but these products are significantly inferior at preventing corrosion to the current chromium (Cr6+ and Cr3+) conversion coatings. While exact formulas are undisclosed, known non-chromium conversion coating solutions are either zirconium-based or cerium-based, and some contain a supplemental soluble, inorganic salt, such as zinc sulfate. Unpainted aluminum 2024 panels treated with these formulas, on average, will last no more than 2-4 days in neutral salt fog (ASTM B117) before showing significant signs of corrosion.

[0008] Based on the current state-of-the-art, there is still a strong need for chromium-free conversion coatings which perform similarly to Cr6+ and Cr3+ products, especially in corrosion resistance of "bare" or unpainted aluminum alloys. This requirement is critical for use in virtually all military and aviation applications and is included in military, commercial, and company specifications for conversion coatings.

[0009] Recent research and development in chromium-free conversion coating is based on the demand for superior products that could be used for bulk applications as well as for treatment of the aluminum powder used in Al-rich primers. One promising area of research is the polycarboxylate compounds used in Al-rich primers. These have demonstrated improvements in corrosion performance when combined in certain ratios and concentrations. These salts have also shown improvements in the corrosion resistance of fluoro-zirconate-based conversion coatings solutions despite their tendency to have low solubility. The fluoro-zirconates are added to the chromium-free conversion composition in amounts ranging from about 4 to 8 grams, e.g., grams per liter of the chromium-free composition. A fluoro-zirconate-based conversion coating without any supplemental inhibitors will provide about 2 days of protection in neutral salt fog before exhibiting signs of corrosion. Adding certain carboxylate inhibitors to this base will increase its protection to 10 days in neutral salt fog, while other carboxylate inhibitors, some of which improve corrosion resistance in primers, will impair the corrosion performance, resulting in significant corrosion after 24 hours in salt fog.

SUMMARY

[0010] The object of the present invention is to provide a non-chromium rust preventive coating for metal such as aluminum which, is capable of corrosion resistance and does not allow development of white rust or pitting on aluminum. A further object is to provide a method of preventing rust and provide a rust-preventive chromium-free conversion coating.

[0011] It is a feature of the invention to provide a process for treating metal surfaces to protect the metal from corro-

sion. The process comprises coating the metal with a chromium-free conversion coating containing from about 4 to 8 grams of a metal fluorozirconate per liter of the chromium-free conversion coating and from about 0.5 to 5.0 grams of at least one carboxylic metal salt per liter of the chromium-free conversion coating.

DRAWINGS

[0012] FIGS. 1*a* to 1*e* shows 2024-T3 aluminum as treated by Bonderite 5200 (3%) and of PPG X-bond (3% by volume) (1*a*) commercially available chromium-free conversion coating, a potassium hexafluorozirconate solution (1*b*) at a concentration of 6 g/L, CFP1 (1*c*), CFP2 (1*d*), and CFP3 (1*e*);

[0013] FIG. 2*a* shows the commercially available non-chromium conversion coating products, Bonderite 5200 (left and middle) and PPG X Bond (right panel, after 48 hours of salt fog (ASTM B117) exposure;

[0014] FIGS. 2*b-e* show the potassium hexafluorozirconate solution (2*b*), CFP1 (2*c*), CFP2 (2*d*), and CFP3 (2*e*) after 48 hours of salt fog (ASTM B117) exposure;

[0015] FIGS. 3*a-c* show 2024-T3 aluminum as treated by Bonderite 5200 at 3% (3*a*), CFP1 (3*b*) a chromium-free conversion coating containing potassium hexafluorozirconate (6 g/L) and zinc oxalate (1.5 g/L) and CFP4 (3*c*);

[0016] FIG. 4*a* shows the Bonderite 5200 panels after 24-hour exposure to ASTM B117; and,

[0017] FIGS. 4*b* and 4*c* show the CFP1 and CFP4 panels, respectively, after 240 hour (10 days) exposure to ASTM B117.

DESCRIPTION

[0018] This invention is the incorporation of carboxylate metal salts in chromium-free conversion coatings for the purposes of increasing corrosion resistance. The compositions of the inhibitor salts are described as follows. Anions include the polycarboxylates chosen from linear and branched aliphatic molecules like oxalate, citrate, tartrate, succinate, malonate and adipate and the like. Cations include zinc, magnesium, manganese, calcium, strontium, zirconium, scandium, yttrium, lanthanum, and other lanthanides like cerium, praseodymium, neodymium, samarium, europium and gadolinium. The choice of anion and cation will influence water solubility as well as the reactivity with the other chemistries involved in the conversion coating solution and/or the metallic substrate.

[0019] The carboxylate metal salts are added to the chromium-free conversion-free conversion coating in amounts ranging from about 0.5 to 5.0 grams per liter and may be added individually or in combination with other inhibitors. Carboxylate inhibitors may be blended with other carboxylate inhibitors using the same cation. For example, but without limitation, zinc oxalate and zinc malonate may be blended, or they may be blended with different cations with the same or different anions. Another example, but without limitation, cerium oxalate and zinc oxalate or cerium oxalate and zinc malonate may be blended. Carboxylate inhibitors may also be combined with soluble inorganic salts with the same cation, such as zinc oxalate and zinc sulfate or they may be blended with different cations with different anions such as zinc oxalate and lithium phosphate.

[0020] Inhibitors may also be blended with different molar ratios to obtain the maximum synergistic performance. This

may range, but without limitation, from relatively low concentrations of a few milligrams per liter to beyond the super saturation point for the carboxylate inhibitor where no more can dissolve in solution.

[0021] The present invention more specifically relates to synergistic metal polycarboxylate combinations and to methods of treating metal to improve the metal's corrosion resistance. The method includes applying to the surface of metal, a chromium-free conversion coating which comprises an effective amount of a synergistic mixture of metal carboxylates. More specifically, but without limitation, a synergistic blend of corrosion inhibitors, consisting of at least two different metal carboxylates, such as polycarboxylics chosen from linear and branched aliphatic molecules like oxalate, succinate, and adipate, and aromatic molecules like phthalate, mellitate and trimellitate and the like. These are specific examples of some molecules. There are many other polycarboxylic acids which can be used for preparing the synergistic combination.

[0022] The cations of the metal carboxylates are identified in the Periodic Table and include, for example, but without limitation, elements chosen from: Group Ia—Lithium, potassium and sodium; Group IIa—Magnesium, calcium, strontium, and barium; Group IIIb—Scandium, yttrium, lanthanum and the other lanthanides; Group IVb—Titanium and zirconium; Group Vb—Vanadium and niobium; Group VIb—Chromium and molybdenum; Group VIIb—Manganese; Group VIII—Iron, cobalt and nickel; Group Ib—Copper; Group IIb—Zinc; Group IIIa—Aluminum, and Group Va—Bismuth.

[0023] FIGS. 1*a-e* show 2024-T3 aluminum as treated by Bonderite 5200 (3%) and of PPG X-bond (3% by volume) and with various additional coatings. FIG. 1*a* shows the additional coating being a commercially available chromium-free conversion coating, while in FIG. 1*b* it is a potassium hexafluorozirconate solution at a concentration of 6 g/L., which is used as the base for the following conversion coating with inhibitors. In FIG. 1*c*, CFP1 is used, which is a subject chromium-free conversion coating consisting of potassium hexafluorozirconate (6 g/L) and a zinc oxalate at a concentration of 1.5 g/L., while in FIG. 1*d* CFP2 is used. This is another chromium-free conversion coating, which contains potassium hexafluorozirconate (6 g/L) and zinc citrate (1.5 g/L) (the same concentration and cation as CFP1 but with a different carboxylate anion), and CFP3. In FIG. 1*e*, another chromium-free conversion coating I is used, also containing potassium hexafluorozirconate (6 g/L) and calcium oxalate (1.5 g/L) (the same concentration and carboxylate anion as CFP1 but a different cation).

[0024] For FIG. 1*a*, the left and middle panels were immersed for 2 minutes in the Bonderite 5200, the left panel had a final rinse after the coating, the middle was dry-in-place. The right panel was immersed in PPG X-Bond for 5 minutes with a final rinse. For FIGS. 1*b-1e*, panels were immersed for, from left to right, 5, 10, and 15 minutes in their respective conversion coatings. All panels were first cleaned for 10 minutes using an alkaline cleaner (Bonderite C-AK 6849 Aero at 18%) at 140° F., and then chemically deoxidized at room temperature for 1 min. using Bonderite C-1C SmutGo NC at 20%. All conversion coating solutions were at room temperature, approximately 75° Fahrenheit.

[0025] According to this set of neutral salt fog data, it is evident that both the carboxylate anion and cation of the inhibitor contribute to the corrosion protection of the sub-

strate. Further salt fog testing was done using zinc oxalate, FIGS. 3a-c below show 2024-T3 aluminum as treated by Bonderite 5200 at 3% (FIG. 3a), CFP1 (FIG. 3b) a chromium-free conversion coating containing potassium hexafluorozirconate (6 g/L) and zinc oxalate (1.5 g/L), and CFP4 (FIG. 3c), the same as CFP1 but with a different doubled concentration of zinc oxalate (3 g/L). For FIG. 3a, from left to right, panels were immersed for 2, 5 and 10 minutes in the Bonderite 5200. For FIGS. 3b and 3c, the left panels were immersed for 5 minutes in the CFP and the middle and right panels for 10 minutes. All panels were first cleaned for 10 minutes using an alkaline cleaner (Bonderite C-AK 6849 Aero at 18%) at 140° F. and then chemically deoxidized at room temperature for 1 min. using Bonderite C-1C SmutGo NC at 20%. All conversion coating solutions were at room temperature, approximately 75° Fahrenheit.

[0026] This invention is directed to a method of providing chromate-free, conversion coatings when coated onto a metal substrate, such as aluminum or aluminum alloy substrates, said coatings are able to withstand hours of salt spray test without detectable corrosion on the metal. Moreover, the corrosion-inhibiting methods do not cause the health hazards associated with hexavalent chromates coatings.

[0027] While this invention has been described by a number of specific examples, it is obvious that there are other variations and modifications which can be made without departing from the spirit and scope of the invention as particularly set forth in the appended claims.

The invention claimed:

1. A process for treating metal surfaces to protect the metal from corrosion which comprises coating the metal

with a chromium-free conversion coating containing from about 4 to 8 grams of a metal fluorozirconate per liter of the chromium-free conversion coating and from about 0.5 to 5.0 grams of at least one carboxylic metal salt per liter of the chromium-free conversion coating.

2. The process of claim 1, wherein at least one of the carboxylic metal salts has an anion or cation different from the other carboxylic metal salts.

3. The process of claim 2, wherein the cation of the carboxylic metal salt is a metal selected from Group II of the Periodic Table.

4. The process of claim 2, wherein the anion of the carboxylic metal salt is selected from the group consisting of oxalate, tartrate, succinate, adipate, phthalate, mellitate and trimellilate.

5. The process of claim 4, wherein one of the carboxylic metal salts is a metal succinate.

6. The process of claim 4, wherein one of the carboxylic metal salts is a metal oxalate.

7. The process of claim 4, wherein one of the carboxylic metal salts is a metal phthalate.

8. The process of claim 4, wherein the metal is selected from the Periodic Table.

9. The process of claim 4, wherein the metal is selected from Group II of the Period Table.

10. The process of claim 1, wherein the carboxylic metal salt is a polycarboxylic metal salt.

11. The process of claim 10, wherein at least one polycarboxylic metal salt has a cation different from the other carboxylic metal salts.

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