

**FRACTAL PATTERNS FORMED BY POLLUTION-  
PREVENTING MICROEMULSION AND BI-LIQUID FOAM  
INKS AT THE AIR-WATER INTERFACE.**

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INKS AT THE AIR-WATER INTERFACE.**

*by*

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*Submitted*

*in fulfilment of the requirements of the degree of Doctor of Philosophy*

*to the*



**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**AUGUST 2017**

*Dedicated to my dear husband, Suresh.*

## **CERTIFICATE**

This is to certify that the thesis entitled “**Fractal patterns formed by pollution preventing microemulsion and bi-liquid foam inks at the air-water interface**” being submitted by **Sudheshna Moka** to the Department of Chemical Engineering, Indian Institute of Technology, New Delhi, in partial fulfilment of the requirements for the award of the degree of **Doctor of Philosophy** in Chemical Engineering, is a record of bonafide work carried out by her. She has worked under my guidance and supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of the thesis.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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**Sudheshna Moka**

## ABSTRACT

Pattern formation at various interfaces has been an area of interest for researchers across many fields. Be it thin film dewetting or bi-layer dewetting of polymers, self-assembly of metal nanoparticles or the ‘orogenic’ displacement of proteins by surfactants in monolayers, the patterns reveal a striking resemblance. Besides their aesthetic appeal, these patterns hold immense potential for manifold applications – optoelectronic, microelectromechanical systems, sensors, biological membranes, microarrays and biosensors, and colloidal lithography.

Among the systems that form patterns at the air - water/aqueous phase interface, systems such as surfactant and protein mixed monolayers, self-assembled metal nanoparticles and micron sized latex particles exhibit fractal patterns. The present work deals with the patterns formed by pollution preventing microemulsion and bi-liquid foam inks at the air-water interface. Both the vegetable oil based inks are absolute zero VOC inks. It is envisaged that the patterns formed by these inks hold great potential for many applications which could also be pollution free.

When a drop of the ink is placed on the surface of water taken in a petridish, it instantly spreads and breaks up into a web-like network pattern. The entire process is very quick and spontaneous; and is a beautiful phenomenon to behold. The patterns reveal a distinct fractal signature and the fractal dimension is strongly dependent on the amount of pigment present in the ink, the type of pigment, and the visco-elastic properties of the ink. At an optimum combination of viscosity and elasticity of the ink the individual filaments in the network are more stable, yielding higher mean fractal dimension. The observed “string of beads” structure of the filaments as well as the storage and loss moduli measurements confirm such a possibility. The closed cells in the network follow a log normal size distribution.

Two distinct scenarios were observed – in one, the patterns emerge right at the periphery of the ink drop, and in the other, the ink drop first spreads as a film and then forms patterns. Using far-field microscopy and high speed imaging, the latter case was observed to be a case of surface tension gradient driven flow (spreading) followed by liquid-liquid dewetting (pattern formation). Though the final patterns seem to be somewhat similar, the present system is quite different from thin film dewetting, as the film is of the order of micrometers, is much more viscous than the ‘bulk’ substrate liquid which is water. Preliminary calculations and comparisons with liquid-liquid dewetting theory proposed by Brochard-Wyart et al. (1993) show a good agreement.

#### References:

Brochard-Wyart, F., Martin, P. and Redon, C., 1993, Liquid/liquid Dewetting. *Langmuir* 9(12): 3682–9

सारांश:

विभिन्न अंतरफलक में पैटर्न (आकृति) की बनावट कई विषय-क्षेत्रों में शोधकर्ताओं के लिए एक रुचि का एक क्षेत्र रहा है। चाहे बहुलक या पॉलीमरों की पतली फिल्म डिपॉजिटिंग हो या दोहरी-परत डिपॉजिटिंग, धातु नैनोकणों की स्वयं-एकत्रीकरण हो या मोनोलायर्स में सर्फैक्टेंट्स द्वारा प्रोटीन का 'ऑरोजेनिक' विस्थापन, पैटर्न (आकृतियाँ) एक आश्चर्यजनक समानता प्रकट करते हैं। उनके कलात्मक आकर्षण के अलावा, ये पैटर्न (आकृतियाँ) विविध अनुप्रयोगों के लिए असीम क्षमताएं रखती हैं - ऑप्टोइलेक्ट्रॉनिक, माइक्रोइलेक्ट्रोमैकेनिकल सिस्टम, सेंसर, जैविक झिल्ली, माइक्रोएरे और बायोसेन्सर, और कोलाइडल लिथोग्राफी।

उन प्रणालियों के बीच जो पैटर्न (आकृतियाँ) बनाते हैं - हवा - पानी/ जलीय चरण अंतरफलक में, प्रणालियाँ जैसे सर्फैक्टेंट और प्रोटीन मिश्रित मोनोलायर्स, कई स्व-एकत्रित धातु नैनोकण और माइक्रोन आकार वाले लेटेक्स फ्रैक्टल पैटर्न (भग्न आकृति) बनाते हैं। वर्तमान कार्य प्रदूषण रहित सूक्ष्ममुद्रण (मिक्रोएमुल्सिव) और द्वि-तरल फोम स्याही के द्वारा हवा - पानी अंतरफलक में पैटर्न (आकृतियाँ) बनाने से सम्बंधित है। दोनों वनस्पति तेल आधारित स्याही पूर्ण शून्य VOC (अब्सोलुट जीरो VOC) स्याही हैं। यह माना जाता है कि इन स्याही द्वारा गठित पैटर्न या आकृतियाँ कई अनुप्रयोगों के लिए बड़ी संभावनाएं रखती हैं जो प्रदूषण मुक्त भी हो सकते हैं।

जब पेटीडिज में, स्याही की एक बूंद पानी की सतह पर रखी जाती है, तो यह तुरन्त फैल जाती है और जाल-जैसे तंत्र पैटर्न (आकृति) में बिखर जाती है। पूरी प्रक्रिया बहुत तेज और तत्क्षण है; और देखने के लिए एक सुंदर घटना है। ये पैटर्न एक अलग फ्रैक्टल (भग्न) हस्ताक्षर प्रकट करते हैं और फ्रैक्टल (भग्न) आयाम निर्भर करता है स्याही में उपस्थित वर्णक की मात्रा, वर्णक के प्रकार और स्याही के विस्को-इलास्टिक (विस्कोकोलिकता) गुण पर। स्याही की चिपचिपाहट और लोचपन के अनुकूलतम संयोजन पर तंत्र के व्यक्तिगत तंतु अधिक स्थिर होते हैं, जो उच्चतर माध्य फ्रैक्टल (भग्न) आयाम प्रदान करते हैं। देखी गई "मोटियों की लड़ी" जैसे तंतुओं की संरचना और साथ ही भंडारण और हानि मापांक माप ऐसी संभावना की पुष्टि करते हैं। तंत्र में बंद कोशिकाएँ लॉग सामान्य आकार वितरण का पालन करती हैं।

दो अलग-अलग परिदृश्यों को देखा गया - एक में, पैटर्न (आकृति) स्याही बूंद की ठीक परिधि पर उभरते हैं, और दूसरे में, स्याही की बूंद पहले एक फिल्म की भाँति फैलती है और फिर पैटर्न (आकृति) बनाती है। दूर-क्षेत्र (फार फील्ड) माइक्रोस्कोपी और हाई स्पीड इमेजिंग का उपयोग करते हुए, परवर्ती मामला को सतही तनाव प्रवणता या 'ढलान' चालित प्रवाह (फैलाना), जिसके बाद तरल-तरल डिपॉजिटिंग (पैटर्न गठन) होने का एक मामला देखा गया। यद्यपि अंतिम पैटर्न कुछ समान दिखते हैं,

वर्तमान प्रणाली पतली फिल्म डिवेटींग की तुलना में काफी भिन्न है, क्योंकि फिल्म माइक्रोमीटर में है, यह 'थोक' सब्सट्रेट तरल से अधिक चिपचिपा है जो पानी है। ब्रोचार्ड-वाइएट एट अल (1993) द्वारा प्रस्तावित तरल-तरल डिवेटींग सिद्धांत के साथ प्रारंभिक गणना और तुलना एक अच्छी सहमति दर्शाते हैं।

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